A
Project Report on

SALT EFFECT ON VAPOUR-LIQUID EQUILIBRIUM FOR THE BINARY SYSTEM METHANOL+ETHYL ACETATE

In partial fulfillment of the requirements of

Bachelor of Technology (Chemical Engineering)

Submitted By

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CERTIFICATE

This is to certify that that the work in this thesis report entitled "salt effect on Vapour-liquid equilibrium for the binary system methanol +ethyl acetate" submitted by Vaibhav Kumar Mehra in partial fulfillment of the requirements for the degree of Bachelor of Technology in Chemical Engineering, National Institute of Technology Rourkela, Orissa, an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge the matter embodied in the thesis has not been submitted to any other University /Institute for the award of any degree.

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ABSTRACT

In the recent time many scientists and technologists have drawn their attention towards the substitution of a solvent with a non-volatile solid salt in azeotropic distillation which alters the relative volatility. But so far, experimentally, little advancement have been made in this field. The salt effect on vapour-liquid equilibrium of the system: Methanol(1) + Ethyl Acetate(2), for constant liquid composition and under the varied concentrations of the two salts-Lithium Chloride(LiCl) and Lithium Bromide(LiBr) have been reported in this present work.

To prefigure a suitable correlation, the salt effect data obtained experimentally is analyzed. A primary estimation of salt effect on the vapour-liquid equilibrium of the binary system has been presented. Salting-in and Salting-out phenomena are also presented. Under the section of previous investigations and literature review, the history and the development of the work done in this area has been reported along with the vapour pressure measurements and VLE data for the boiling systems.

A modified othmer still, a bulb condenser, a magnetic stirrer-cum heater and a glass thermometer forms the experimental setup and refractive index method has been used for vapour composition analysis, with the help of a digital refractometer with the prism temperature, maintained constant at 20°C i.e. nDt. Activity coefficient has been calculated using the experimental data which is further used in determining theoretical VLE data that can be further correlated with the experimental one to find thermodynamic consistency.

The effect of two inorganic salts-lithium chloride and lithium bromide on the vapor-liquid equilibria (VLE) has been investigated under the atmospheric conditions of 98.6 ± 0.03 kpa pressure. In the present study it has been found that the system forms a minimum boiling azeotrope at 0.732 mole fraction of methanol at 62.6°C. The azeotrope shifts from 0.732 to 0.629, 0,586, 0.472 and 0.471 by addition of 5%, 10%, 15% and 20% of lithium chloride by weight of methanol respectively and to 0.774, 0,706, 0.682, 0.670 by the addition of 5%, 10%, 15% and 20% lithium bromide by weight of methanol respectively. So this was concluded that by using both the salts at different concentrations e.g. 5%, 10%, 15% and 20% by weight, there was a change in relative volatility in the system and the salts were unable to eliminate the azeotrope of the system.

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NOMENCLATURE

G^E = Excess Gibbs Energy

γ_i = Activity Coefficient for Component i

x_i = Mole Fraction of Component i in liquid phase

y_i = Mole Fraction of Component i in vapour Phase

A_{ij} = Constants in Margules Equation

A'_{ij} = Constants in Van Laar Equation

Λ_{ij} = Constants in Wilson Equation

T_{ij} = Constants in NRTL Equation

y_i^* = Theoretical vapour phase mole fraction of component i

x_i^* = Theoretical liquid phase mole fraction of component i

R = Ideal Gas Constant

T = Temperature (K)

P_i^{sat} = Saturated vapour pressure of component i

P^T = Atmospheric Pressure (98.6 ± 0.03 kpa in Rourkela)

A, B, C = Antoine's Equation Coefficients

i, j, k = Component Identification

u_x = Refractive index

CHAPTER 1

INTRODUCTION

1.1 Introduction

Vapour-liquid equilibrium (**VLE)**, is a condition where a liquid and its vapour (gas phase) are in equilibrium with each other or more precisely a state where the rate of evaporation equals the rate of condensation on a molecular level such that there is no overall vapor-liquid inter-conversion.

Whenever a mixture of liquids is boiled, the composition of the vapor phase is usually different from that in the liquid phase. For some mixtures there is a unique point or rather composition where the liquid and vapor phases are identical, these kinds of mixtures are known as the azeotropes. The azeotrope may have a boiling point higher than the boiling point of the two pure liquids from which it is formed and are known as maximum boiling point azeotrope or lower than the boiling point of the two pure liquids from which it is formed and therefore referred as minimum boiling point azeotrope. In a maximum boiling point azeotrope the intermolecular forces between different molecules are stronger than the forces between either of the pure forces, whereas in a minimum boiling point azeotrope the intermolecular forces between different molecules are weaker than the forces between either of the pure forces. [24]

In many branches of science, the phase equilibrium thermodynamics is of fundamental importance. In chemical engineering almost all the manufacturing processes involve mass and energy transfer between phases. Processes such as: gas – liquid absorption, adsorption, leaching, refrigeration, distillation, liquid – liquid extraction etc. are some of important areas where mass transfer and heat transfer between phases are taken very effectively into account to get desired result.

The separation of azeotropic systems (which have low relative volatility) is either difficult or uneconomical, by using conventional methods like fractional distillation .To overcome such difficulties in industries a third component is added in order to alter the system properties. If the third component is liquid then in that case the molecules of the liquid component forms an association or complex with the molecule of the less volatile component of the feed as compared to that of the more thereby increasing the relative volatility of the more volatile component and thus the azeotrope can be eliminated. This process however requires an additional column to recover the separating agent from the product stream. [20]

Due to this difficulty the solids salts are considered better than the liquid separating agents as they produce a solvent-free extract and requires no other separating column. The salt dissolved in a mixed solvent may affect the boiling point, the mutual solubilities of the two liquid components, and the equilibrium vapour phase composition. Generally, the ions of the dissolved salt tend to attract, the molecules of the more polar component by the electrostatic field of the ions and thereby enriching the vapour composition of the less polar solvent, in which the salt is less soluble.

If the dissolved salt associates, preferentially, with the molecules of one component of the solvent compared with those of the other, then in that case one component is "salted out" in respect to the other. In such a case, the activities and the solubility relationship between the two volatile components of the liquid solution are altered relative to each other in a manner which results in a change of composition of the equilibrium vapour phase, even if no salt is present in the vapour phase.

Various predictive and correlative models were proposed to calculate the vapour-liquid equilibrium of the mixed solvent-salt systems. The experimental data are correlated using four models based on the local composition concept:

1-The electrolytic NRTL model of Mock et al. (1986)

2-The modified UNIQUAC model of Sander et al. (1986)

3-Modified Wilson and modified NRTL models of Tan (1985), Tan (1987) and Tan (1990).

The results of correlation were compared with those obtained through data prediction using the modified Wilson and the modified NRTL predictive models of Tan. The new set of ion-solvent and salt-solvent interaction parameters obtained from the data correlation with the extended UNIQUAC model of Sander et al. (1986) and salt-solvent interaction parameters obtained from the data correlation with the electrolyte NRTL model of Mock et al. (1986), would be a contribution to the database.[12,19]

1.2 Applications

Distillation in industries is mainly based on the fact that the composition of vapour should be different from that of the liquid and side by side must have high relative volatility with which it is in equilibrium. As discussed above, the effective and

economical separation of components for the system showing azeotrope formation is done by extractive distillation and/or azeotropic distillation using salt as a third component. Salt is neither vaporized nor condensed anywhere in the distillation process and therefore has low energy requirements. This type of process using salt in extractive distillation was first applied in

- HIAG (Halz industries Acetin Geselleschoft) process; it was licensed by DEGEUSSA and based on patents registered by Adolph Gorhan. [21]. HIAG process used extractive distillation where 70/30 mixtures of the potassium and sodium Acetate were used as separating agent. It produced around 99.8% Ethanol, completely free from the separating agent and obtained directly from the top of the column. This process had a lower capital investment and energy cost than azeotropic distillation benzene is used as an agent.

- Azeotropic distillation involving benzene was also the conventional process for Isopropanol-water separation. The IHI (Ishika Wajima-Harima heavy Industries) company in japan [13,15] was implementing a process for production of alcohol from its aqueous solution the salt calcium chloride to break the azoetrope, by this process the company is having a production capacity of 7300 tones per year which further reducing the capital cost to 56% and an energy requirement to 45% of that of the conventional benzene process.

- The only large scale production by use of salt effect on extractive distillation in North America was production of nitric acid from aqueous using magnesium nitrate as separating agent.

- In 1926 Othmer [4] developed a large-scale industrial process for Eastern Kodak, which separated methanol from its aqueous azeotrope by extractive distillation using strong calcium chloride, brine as separating agent. Rather than patenting the process, Eastern decided instead, to have it remain as trade secret. He also experimented with the use of salt as separating agent for the concentration of acetic acid from its aqueous solution.

1.3 Effect of dissolved salt in boiling solution

A salt dissolved in a boiling solution of a binary system; there are several expected effects which may occur. They are as follows

- There is crossover in salt effect between salting- out and salting-in, as liquid composition is increased, even though the salt is clearly more soluble in one of the components of the binary system.

- There is an enrichment of vapor composition through out, in the component in which salt is less soluble than that of other.

- There is a relatively large effect on vapor composition caused by a salt having little difference in solubility between the components.

The overall effect is the net change in the relative volatility or shifting of the azeotropic point or the elimination of the azeotrope, if the selection of the salt is proper [22].

1.4 Theories of Salt Effect

1.4.1 Electrostatic Effects - Debye and McAuley [1] were the first to treat salting out as an electrostatic phenomenon. They considered the ion as a perfect sphere**,** they defined a Helmholtz work function, **ΔA,** is equal to the difference in the work of charging and discharging the ion in the media of dielectric constants say, **D** and $\mathbf{D_0}$**,** respectively, and the work done against the potential due to the ionic atmosphere. They expressed the activity coefficient of the non-electrolyte as a function of the ratio of charge to ionic radius, the ion concentration, and the decrement in the dielectric constant of the aqueous solution due to non-electrolyte. The equation of Debye and McAuley is based upon the assumptions that the dielectric constant of the solution can be expressed as a linear function of salt concentration and non-electrolyte concentration; salting out is due only to alterations in the dielectric constant of the solution; and the solution is dilute in both non-electrolyte and salt. Estimation of the ionic radius in solution is very difficult, especially at moderate to high ion concentrations. The electrostatic theory gives fairly good results for many dilute systems. However, it always predicts salting out and cannot account for salting in [10].

1.4.2 Van der Waals Forces- Electrostatic attractions between ions and a neutral molecule are to large extent short-range forces. Other short-range forces, such as dispersion forces, may also be of considerable importance. Long and McDevit [6] proposed the semi empirical equation

$$\ln \gamma' = A \sum (Z_j)^2 C_j - B \sum a_j C_j \qquad \text{.....(1.1)}$$

Where,

A and **B** = empirical constants dependent upon both non-electrolyte and electrolyte

a_j = polarizability of ion **j**

C_j = molar concentration of ion of type **j**

Z_j = valence of ion of type **j**

The first term in Equation **1** accounts for changes in the activity coefficient due to electrostatic interactions; the second term reflects the effect of dispersion forces [10].

1.4.3 Solubility of Salts in Non-electrolyte- If a salt is more soluble in the non-electrolyte than in water, salting in will occur. Glasstone [2] noted an increase in the solubility of ethyl acetate in water when lithium and ammonium iodides were added. These iodides are more soluble in ethyl acetate than in water. The salting in may be due to a preferential association of ions and non-electrolyte or of undissociated salt and non-electrolyte, A general analysis of the salt effect indicates that salting out decreases with rising dipole moment, that hydration effects are scalar for non-polar, but vector for polar non-electrolytes, large ions cause small salting in due to hydrotropism; and salting in results when a salt is more soluble in the non-electrolyte than in water [10].

1.4.4 Hydration Theory-The hydration theory was proposed by Rothmund [23].He postulated that each salt ion binds a constant number of water molecules as a shell of oriented water dipoles surrounding the ions, thereby decreasing the activity of the water but having no effect on the remaining water or on the non-electrolyte . This "bound" water is then unavailable as solvent for the non-electrolyte. The number of water

molecules so bound by each salt ion is called the hydration number of the ion. Considering the wide variation in hydration numbers reported in the literature, it appears that this concept permit only a qualitative estimate of the magnitude of the salt effect, Mc.Devit [5] found this model is inadequate because it indicated the hydration number, which should be independent of the species of non-electrolyte, which is not true. Also this theory neither allowed the occurrence of salting-in nor did it correspond to the observed ion order.

The hydration theory, however, has considerable success when it is applied to aqueous solutions of non-electrolytes for potentially ion-sizeable polar non-electrolytes; harned and owen have proposed the modified hydration theory. This theory explains the differences in effects due to solutes and ions by assuming that each on orients water molecules in a definite direction. If the orientation is favorable to the non-electrolyte molecules, salting-in occurs; an unfavorable orientation reduces salting-out [22].

1.4.5 Internal Pressure- According to the internal pressure concept proposd by Tammann and applied Mc.Devit and Long [5], the concentration in the total volume upon the addition of salt to water can be thought of as a compression of the solvent. This compression makes the introduction of a molecule of non-electrolyte more difficult, and this result in salting-out. An increase in total volume upon the addition of a salt would produce the counter effect known as salting-in.

Mc. Davit and Long [5] applying and internal pressure concept of Tammann to non polar non-electrolytes, calculated the free energy of transfer of latter from pure to the salt solution [22].

CHAPTER 2

LITERATURE REVIEW AND PREVIOUS INVESTIGATIONS

2.1 Effect of Salt on Vapour-Liquid Equilibrium

The addition of a dissolved salt is generally known to further complicate the vapour-liquid equilibrium relationships in a system of two volatile components, since the liquid phase then becomes a concentrated solution of an electrolyte whose degree of dissociation is a function of the relative proportions of the other two components. The salt may affect the activities of the volatile components either through formation an association complex or alternatively altering the structure of the binary solvent mixture. Generally, the particles (molecules or ions or both) of dissolved salt tend to attract the molecules of one component of the binary more strongly than those of the other, tending to form association complexes preferentially, but not necessarily solely, with the former. Usually, the added component is more likely to associate preferentially with the chemically similar binary system (like associates with like), thus affecting the volatilities of the two original components by differing amounts.

Electrostatic fields by preferential attraction of the salt ions would apply for the more polar component of the binary solvent. Since the added agent is likely to complex to a certain extent with both liquid components, the volatiles of both will most likely tend to be lowered, but by differing amounts depending on how selective the agent is, if the association preference of the salt is for the less volatile of the two liquid components, then its volatility will be reduced by volatile component, resulting in an increase in the value of relative volatility and enrichment of the equilibrium vapour in the more volatile component. Also, the value of relative volatility will be decreased and the vapor composition will be enriched in the less volatile component if the association preference of the salt is for the more volatile component.

A general rule of thumb used often in Physical Chemistry states that like dissolves like. That is, the things tend to be most soluble in those solvents with which they are most similar to in terms of their molecular nature and structure. When like dissolves like is coupled with like associated with like, the empirical rule of salt effect theory results which predicts that the vapour phase will be enriched in that component of the binary solvent in which the salt is less soluble. In other words, if the salt more soluble in the less volatile component, the salt will increase the value of relative volatility. Conversely, if

the salt is more soluble in the more volatile component, relative volatility will be decreased. In the former case, the more volatile component is said to be salted out by the salt, and in the latter, to be salted-in. Previous experimental findings have tended to support the above theory of salt effect as general.

Kablukov and Miller were amongst the first to study the ethanol water system with various salts added. Gross and Halpern refined the liquid phase model relating salt effect on vapor composition to association in the liquid phase. Empirically, it has been concluded that the magnitude of salt effect on the activity coefficients of the volatile components, for a given salt in a given system, will depend on the concentration of salt present in solution, and on salt effect parameter (Further, Johnson and Furter)[3,8] which is a function of such factors as degree of difference of solubility of the salt in the two pure components, degree of dissociation of the alt in solution, ion charge, ion radius, and others [22].

2.2 Theories and Literature Survey

One needs to be well versed with the basic thermodynamic properties and assumptions, which directly or indirectly affect the vapour liquid equilibrium and inter conversion of energies of the system before going into experimentation. Determination of the thermodynamic properties of a fluid that cannot be measure directly necessitates relating such properties to measurable quantities. The relationships formulated between the thermodynamic properties and the measurable quantities facilitate for easier calculation of the phase equilibrium for industrial practice. Some of the literature on different experimental results and theories behind it are as follows.

2.3 PREVIOUS INVESTIGATIONS

Many authors have worked on the salt effect on vapour-liquid extraction system. It is observed that the use of salt has proven advantageous. Although a relative few significant advances and developments in this field is reported at experimental level. In this review developments and trends are outlined with emphasis on existing correlation. The systems with the results obtained by different authors are listed below.

2.4 LIST OF SOME PREVIOUS INVESTIGATION ON SALT EFFECT ON VLE

S.NO	Reference	SYSTEM	SALT USED	CONCLUSIONS
1	Fawzi banat, Sameer Al Aseh, Jana Simandl - effect of dissolved inorganic salts on VLE.	Propionic acid-Water mixture	NaCl, NH_4Cl, & $AlCl_3$	The VLE of the propionic acid-water system under no-salt condition and in the presence of four chloride salts (NaCl, NH_4Cl, $CaCl_2$, $AlCl_3$) dissolved to various concentrations were studied at 40 and 50.8°C. The chloride salts used in this work have a salting-out effect on propionic acid in the following order: $AlCl_3$> $CaCl_2$> NaCl> NH_4Cl. The enhancement factor was mainly dependent on the salt type and concentration, rather than on temperature. Increasing salt concentration led to the increase of salting-out of propionic acid. Experimental data were well correlated by the modified Furter equation.
2	Tongfan Sun, Kerry R. Bullock, Amyn S. Teja- Correlation and prediction of salt effects on vapor–liquid equilibrium in alcohol–water–salt systems	Ethanol-Water	KI, NaCl, $CaCl_2$	A modified solvation model is described for the correlation and prediction of salt effects on VLE in alcohol–water–salt systems. The model incorporates the Bromley equation to calculate the water activity, to describe alcohol–salt interactions. The modified solvation model yields results that compare well with experimental data and with published models.
3	T.C.Tan,C.M.Chai, A.T.Tok, K.W. Ho -Prediction and	Water–Ethanol–2-Propanol mixture	$NaNO_3$, NaCl, KCl	The vapour–liquid equilibrium of water–ethanol–2-propanol was experimentally found to be

	experimental verification of the salt effect on the vapour–liquid equilibrium			affected by the addition of $NaNO_3$, NaCl, KCl or CH_3COOK. All these salts salted-in water more than ethanol and 2-propanol and all except NaCl salted-in ethanol relatively more than 2-propanol. These effects were well predicted by Tan–Wilson and Tan–NRTL models
4	Shuzo Ohe, Kimihiko Yokoyama and Shoichi Nakamura	Acetone-Methanol	KI, NaCl, $MgCl_2$, $CaCl_2$	If the salt is more soluble in a less volatile component, then the relative volatility will be raised, because of the lowered vapor pressure of the less volatile component. The salts are more soluble in methanol, the less volatile and thus increasing relative volatility. On the other hand, the salt effect increases with increasing solubility ratio of salt in acetone to methanol at the concentration from 60 to 100 mole %acetone.
5	Ernesto Vercher, A.Vicent Orchill´es,Pablo J. Miguel, Vicenta Gonz´alez-Alfaro, Antoni Mart´ınez-Andreu-Isobaric vapor–liquid equilibria at 100 kPa	Acetone+ Methanol	Lithium Nitrate	The addition of lithium nitrate to acetone + methanol system produces an important salting-out effect on the acetone, and the azeotrope disappears at salt mole fractions higher than 0.022. This effect is stronger than that produced by sodium iodide, sodium thiocyanate, and calcium bromide on this system.
6	A. Vicent Orchill´es, Vicenta Gonz´alez-	1-propanol +water	copper(II) chloride	The addition of copper(II) chloride to 1-propanol +water systems produces a salting-out effect of the alcohol and the

	Alfaro, Antoni Mart´ınez-Andreu-Isobaric vapor–liquid equilibria at 100 KPa			displacement of the azeotropic point towards higher *x*1 values. This effect is smaller than that observed for calcium nitrate, calcium chloride, lithium nitrate, or lithium chloride on this system. On the other hand, the minimum non-azeotropic point also changes with the salt content but this variation is small and does not depend, practically, on the salt used.
7	Michael Jo1decke, A lvaro Pe´rez-Salado Kamps, and Gerd Maurer-	Methanol+ water	NaCl	By increasing the concentration of the salt in the liquid (at constant temperature and at constant salt-free concentration of methanol in that liquid), an increase in the concentration of methanol in the gaseous phase is experimentally observed (i.e., methanol is “salted-out”, and water is “salted-in”).
8	Maria C. Iliuta l, Fernand C. Thyrion	acetone+ methanol	Sodium Thiocyanate, NaI.	In the acetone-methanol-NaSCN system, a crossover effect between salting-in and salting-out on acetone was observed as in the case of NaI, the transition from salting-in to salting-out takes place at an acetone mole fraction (salt-free basis) of about 0.3 for the NaSCN and 0.2 for the NaI system. In the case of NaSCN, the azeotropic point can be eliminated at a salt mole fraction higher than 0.03. A stronger salting-out effect and a weaker salting-in effect on acetone was observed in NaI compared to NaSCN. An apparent crossing point between the dew point and the

				bubble point curves was also found for the acetone-methanol-NaSCN system, as in the case of NaI.
9	A. S. Narayana, S. C. Naik, and P. Rath -Salt Effect in Isobaric Vapor-Liquid Equilibria	Acetic Acid+Water	KCI, Na_2SO_4, and K_2SO_4	Addition of KCI, Na_2SO_4, and K_2SO_4 results in "salting out" of acetic acid. Water-acetic acid solutions containing salts KCI and Na_2SO_4 above 80 and 91wt % water on salt-free basis, respectively, form azeotropes. An equation of the type log **(**Ys/Y_0**)** = KW fits the data for the three salts studied in this system. All the three salts studied are found to have salting out effect for acetic acid in varying degrees.
10	S. Abderafi and T. Bounahmidi Measurement and estimation of vapor–liquid equilibrium for industrial sugar juice using the Peng–Robinson equation of state .	Sucrose, glucose, fructose, aspartic acid, glutamic acid, acetic acid, lactic acid and succinic acid	NaOH and KCl	In the present study, attention is given to adapting the PR EOS for industrial sugar juices using the pseudo component approach. Industrial sugar juices were considered as aqueous solutions of sugar, amino acid, carboxylic acid and ash. The pseudo components composition can be obtained by analytical techniques frequently used in sugar industry. In future papers, the PR EOS will be used to predict other physical properties of industrial sugar juices and to simulate evaporation process of a sugar factory.

11	Motoyoshi Hashitani and Mitsuho Hirata-salt effect of calcium chloride in vapour-liquid equilibrium of alcohol-acetic ester systems	Ethyl acetate+ ethanol	Calcium chloride	The increase of relative volatility of acetic ester is noticed when calcium chloride is added in these alcohol-acetic ester mixtures. The azeotropic composition of these mixtures shifts to the higher acetic ester composition. The addition of calcium chloride is suggested to be effective for the separation of these alcohol-acetic ester mixtures.

CHAPTER 3

DETERMINATION OF VLE DATA

3.1 Experimental Determination of vapour-liquid Equilibrium

Various methods for direct determination of equilibrium data are as follows:

1. Distillation method
2. Circulation method
3. Static method
4. Bubble and Dew point method
5. Flow method

The present experimental setup is based on the circulation method, so the basic theme of the setup and procedure the method is as follows.

3.1.1 Distillation Method

In this method, liquid is taken in the boiling flask and heated, as the composition of liquid phase is constant, a small amount of liquid is considered for analysis. Condensation of the vapour on the cold walls of distillation flask at the beginning of the experiment leads to large number of errors, that's why this method is seldom used.

3.1.2 Circulation method

This method is the most commonly used, can easily be used both in the region of medium and low pressure. Various equilibrium stills with simple circulation differ significantly in their construction details but they all are based on a common principle.

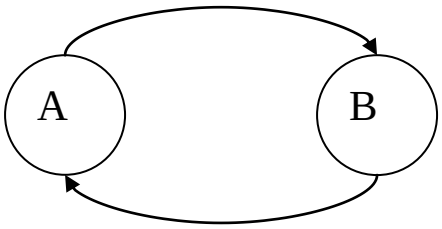

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Fig-1 Schematic diagram for circulating stills

Principle

As the vapors come out from the distillation flask ‘A’ they pass through the vapour conduit and after complete condensation collect in the receiver ‘B’. The liquid flows backward once the receiver is filled; a trap is generally inserted there to prevent the flow of liquid from the distillation flask to the receiver. If the still is started with the receiver B empty, at the instant at which it fills, its contents are richer in more volatile component than that of the vapour phase over the boiling mixture in the distillation flask. Operating further, the contents of the distillation flask become richer with more volatile component and the receiver becomes poorer. This process continues till the steady state is obtained, in which the compositions in both vessels no longer changes with time. Both compositions are determined automatically.

According to the manner of circulation of the phases, these stills are classified into two groups.

1. Still with circulation of the vapour phase.
2. Still with circulation of the vapour and liquid phase.

These stills with minor modifications have been used in the present experimental work.

3.2 Othmers Still and its Modification

Othmers still was designed and constructed D.F. Othmers [4] in 1928. The Still is made of glass, so it is quite compact. Due to some faults and vulnerability, certain modifications were made in the design and construction.

An improved version of othmers still was presented by Johnson and Futer [9] for the salt effect studies. Fig-2 shows such equilibrium still. The modifications introduced are

a) Flattening the bottom of still to facilitate the use of magnetic stirrer-cum plate heater.
b) Introduction of a thermowell or protector of thermometer, to prevent the accidental knocking of the thermometer by the stirrer.

The still was lagged with two layers of the magnesia-asbestos covering the boiling chamber from the liquid level to tire top of the neck [22].

3.3 Procedure for Determination of VLE Data

Apparatus and procedure

The still which was used in the present work had been designed to avoid and reduce faults and errors. The still was thoroughly washed with water and then with methanol. It was mounted over the hot plate magnetic stirrer. A condenser was mounted over the condensate chamber. A magnetic stirrer was used for stirring thereby maintaining homogeneity of the liquid to improve salt dissolution.

The main characteristic of the present design is that, the pot volume is much higher than the liquid condensate volume and at steady state only a few drops of condensate were collected and analyzed for the determination of the vapour composition. Due to which the composition of the liquid prior to the addition of the salt could well be taken as the equilibrium liquid composition without introducing appreciable error. The still was charged with 200 ml of methanol and ethyl acetate mixture of desired composition.

So, let us suppose

Volume of methanol be ‘v’ ml

So volume of ethyl acetate= ‘(200-v)’ ml

If n is the mole fraction of methanol, then

$$n = \frac{(\rho_m * v/Mm)}{(\rho_m * v/Mm + \rho_e * (200-v)/M_e)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

ρ_m=density of methanol

ρ_e=density of ethyl acetate

Mm=molar mass of methanol

M_e=molar mass of ethyl acetate

TABLE 1-Data of the amount of methanol and ethyl acetate added in ml

Mole fraction of methanol	Volume of methanol (ml)	Volume of ethyl acetate (ml)
0.1	8.84	191.16
0.2	18.85	181.15
0.3	30.28	169.72
0.4	43.45	156.55
0.5	58.78	141.22
0.6	76.89	123.11
0.7	98.55	101.45
0.8	124.96	75.04
0.9	157.89	42.11

TABLE 2- Data of the amount of salt added in gms

Weight of methanol in gms. (W)	5% of W in gms	10% of W in gms	15% of W in gms	20% of W in gms
6.9535	0.3477	0.6954	1.0431	1.3908
14.8305	0.7415	1.4830	2.2245	2.9660
23.8197	1.1909	2.3818	3.5727	4.7636
34.1782	1.7089	3.4178	5.1267	6.8356
46.2439	2.3122	4.6244	6.9366	9.2488
60.4848	3.0242	6.0484	9.0726	12.0968
77.5202	3.8760	7.7520	11.6280	15.5040
98.2951	4.9148	9.8296	14.7444	19.6592
124.2002	6.2100	12.4200	18.6300	24.8400

Now the set up is ready for operation at an atmospheric condition of 98.6±0.03 kpa, pressure. The thermometer was introduced into the respective port as shown in the Fig 2. The energy control switch regulator ensures continuous stirring and uniform heating. The solution was heated for some time till the condensate was observed. Then again the solution was allowed to heat at a milder heating than before till the steady state was reached i.e. the temperature in the thermometer became constant. The solution is again heated for about 30 minutes to ensure the attainment of equilibrium a few drops of vapour sample were collected for analysis.

As the vapour sample withdrawn for analysis, is negligible, the original composition of the liquid practically remains unchanged, which was taken as liquid phase composition without including any substantial error.

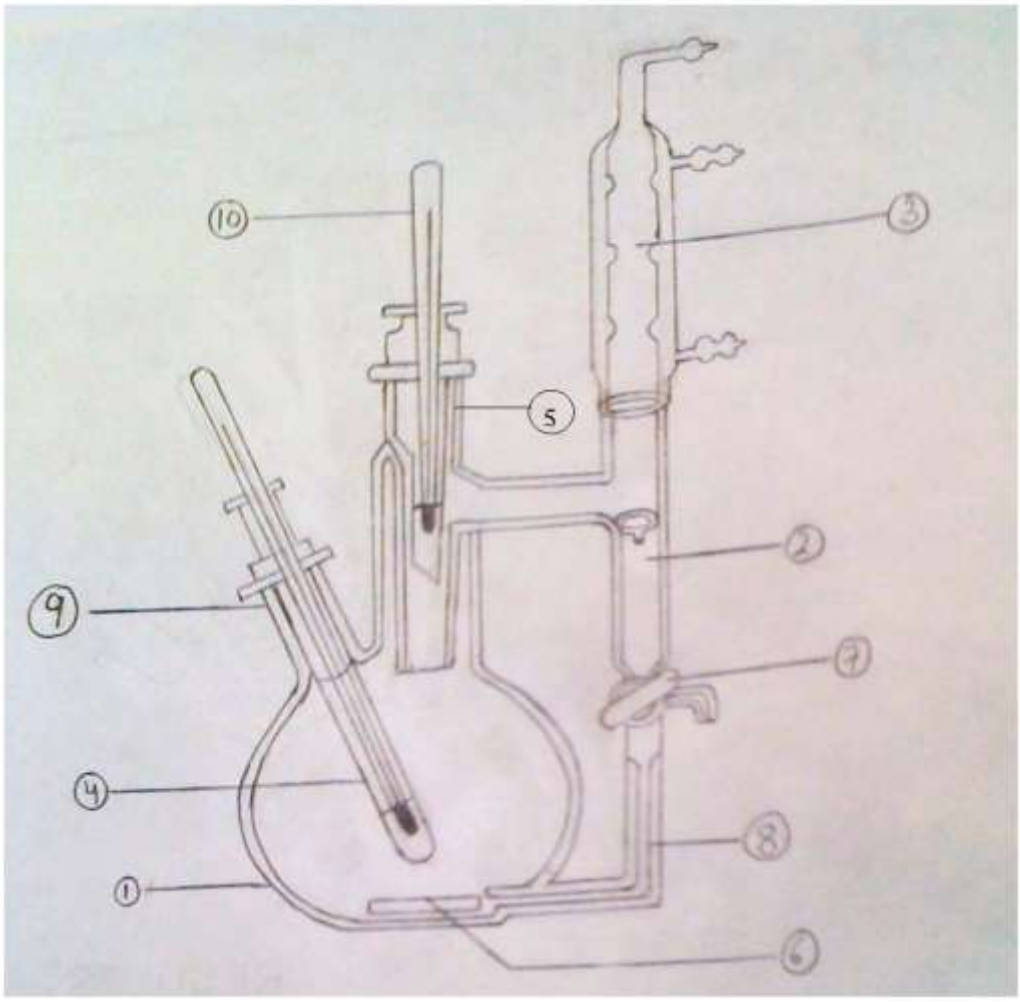
TABLE 3 - Physical properties of solvents used

Components	Boiling Points in °C		Refractive Index at 20°C		Specific Gravity 20°C	
	Present work	Literature*	Present work	Literature*	Present work	Literature*
Ethyl acetate	77.1	77	1.3689	1.3766	0.899	0.899
Methanol	64.7	64.7	1.3265	1.3302	0.790	0.790

***** International critical Table

3.4 Method Analysis

The method of analysis of the vapour sample, which was considered to be completely free from the dissolved salt, involved either the physical properties determination like density measurement or refractive index measurement or instrumental method of analysis like gas chromatography. However all the samples were measured by the refractive index method. Using a digital refractometer whose prism temperature was maintained constant at 20°C.



1. **Boiling Chamber**
2. **Condensate Chamber**
3. **Bulb Condenser**
4. **Thermowell**
5. **Thermowell**
6. **Magnetic Bar**
7. **Three Way Stopcock**
8. **Capillary Tube**
9. **Salt Loading Port**
10. **Thermometer**

VLE APPARATUS

Fig 3 - VLE Apparatus (Still)

REFRACTOMETER

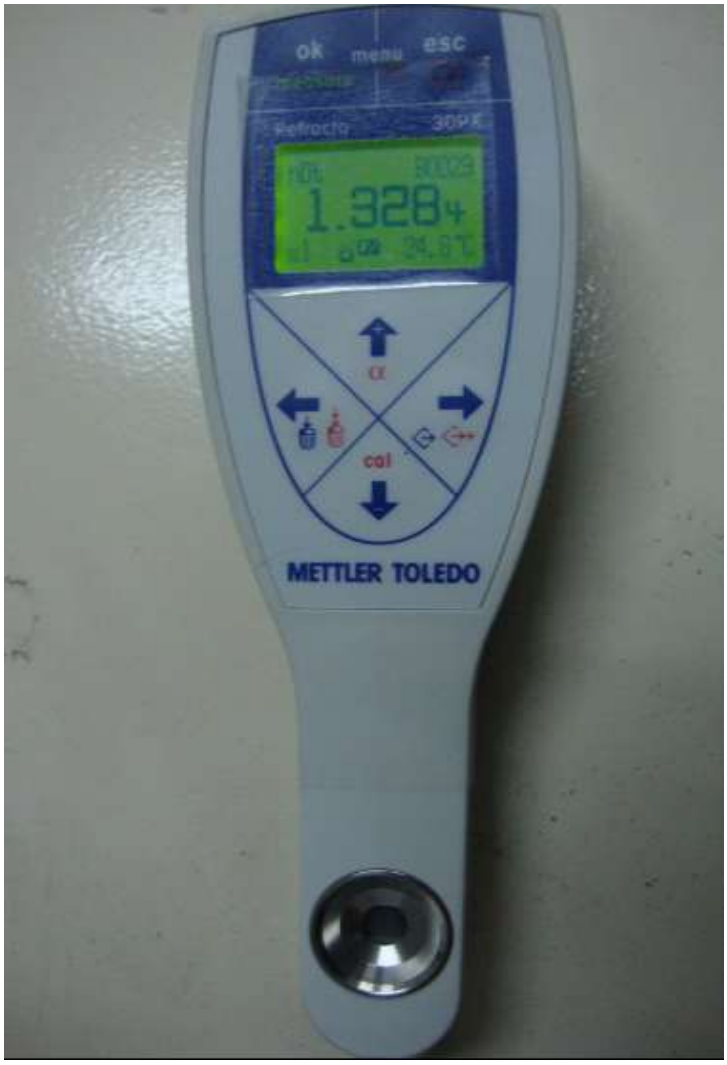


Fig 4 -Refractometer

CHAPTER 4

TREATMENT OF VLE DATA

This chapter represents the analysis of the experimental work. The isobaric VLE data determined and tabulated has been investigated. In this chapter we examine what can be learned from the experiment. Consider the measurements of vapour-liquid equilibrium data, from which activity coefficient correlations are derived.

4.1 Computation of Vapour-Liquid Equilibrium

Experimental VLE measurements contain some combination of the measurable variables like temperature, pressure and vapour or liquid compositions. Static equilibrium stills, for example may produce either P T x, P T y or P T w (weight of the component in system). As all the important variables are not measurable, so they can be derived by computation. However in re-circulating stills, all four variables are measurable but one of them can be excluded for computation.

4.2 Model-Dependent method for Data Reduction

This method is applied for a reduction of P T x – equilibrium data, using model for the excess Gibbs free energy as a function of composition. As a result model parameters are obtained, and the composition of vapour phase can be calculated from the known composition of other phase at any desired temperature or pressure within a valid range.

4.3 Models for excess Gibbs Energy

In general GE/RT is a function of T, P and composition, but for liquids at low to moderate pressures it is a very weak function of P. Therefore the pressure dependence of activity coefficient is usually neglected. Thus, for data at constant T:

$$G^E/RT = g(x1, x2, x3\ldots, xn) \quad (\text{const T})$$

The "Margules equation" is an example of this functionality, which is given by

$$\ln \gamma_1 = x_2^2[A_{12} + 2(A_{21}-A_{12})x_1] \qquad \ldots\ldots\ldots\ldots\ldots\ldots(4.1)$$

$$\ln \gamma_2 = x_1^2[A_{21} + 2(A_{12}-A_{21})x_2] \qquad \ldots\ldots\ldots\ldots\ldots\ldots(4.2)$$

A number of other equations are in common use for correlation of activity coefficients. For binary systems the function is represented by an equation is GE/x_1x_2RT, which may be as a power series in x_1;

$$G^E/x_1x_2RT = a + bx_1 + cx_1^2 + \ldots \text{ (Const T)}$$

As $x_2 = 1-x_1$ mole fraction x_1 serves as the single independent variable. An equivalent power series with certain advantages is known as Redlich/Kister expansion [7]

$$G^E/x_1x_2RT = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots$$

In application, different truncations of this series are appropriate and in each case specific expressions for $\ln \gamma_1$ and $\ln \gamma_2$ are generated by the following equation.

$$\ln \gamma_1 = [\partial(nG^E/RT)/\partial n_i]_{P,T,n_j} \qquad \ldots\ldots\ldots\ldots\ldots (4.3)$$

When A=B=C= ....=0, $G^E/RT=0$, $\ln \gamma_1 = 0$, $\ln \gamma_2 = 0$, $\gamma_1=\gamma_2=0$, and the solution is ideal .

If B=C=…..=0, then

$$G^E/x_1x_2RT = A$$

Where 'A'is a constant for the for a given temperature. Corresponding equations for $\ln \gamma_1$ and $\ln \gamma_2$ are

$$\ln \gamma_1 = Ax_2^2 \quad \text{and} \quad \ln \gamma_2 = Ax_1^2$$

Infinite-dilution values of the activity coefficient are $\ln \gamma_1^{\infty} = \ln \gamma_1^{\infty} = A$
If $C = \ldots = 0$ then

$$G^E/x_1x_2RT = A + B(x_1 - x_2) = A + B\,(2x_1 - 1)$$

In this case G^E/x_1x_2RT is linear in x_1. if we define $A+B=A_{21}$ and $A-B=A_{12}$, the Margules equation obtained,

$$G^E/x_1x_2RT = A_{21}x_1 + A_{12}x_2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots (4.4)$$

Another well known equation results when the reciprocal expression is expressed as a linear function of x_1,

$$\frac{x_1 x_2}{G^E/RT} = A' + B' (x_1 - x_2)$$

This may also be written as

$$\frac{x_1 x_2}{G^E/RT} = A'(x_1 + x_2) + B' (x_1 - x_2)$$

The new parameters are defined as A'+ B' =1/ A'12 and A' - B' =1/ A'_{21}

so an equivalent form is obtained :

$$\frac{x_1 x_2}{G^E/RT} = x_1/ A'_{21} + x_2/ A'_{12} \qquad \text{..... (4.5)}$$

$$G^E/x_1x_2RT = \frac{A'_{12}\, A'_{21}}{A'_{12}\, x_1 + A'_{21}\, x_2} \qquad \text{..... (4.6)}$$

The activity coefficient implied by this equation is

$$\ln \gamma_1 = A'_{12} \left(1 + \frac{A'_{12}\, x_1}{A'_{21}\, x_2} \right)^{-2} \quad \text{and} \quad \ln \gamma_2 = A'_{21} \left(1 + \frac{A'_{21}\, x_2}{A'_{12}\, x_1} \right)^{-2}$$

These are known as van laar equations. When x_1=0, $\ln \gamma_1^{\infty} = A'_{12}$ when x_2=0,

$\ln \gamma_2^{\infty} = A'_{21}$

The Redlich/Kister expansion, the Margules equations, and the van laar equation are all special cases of a general treatment of based on rational functions, i.e. on equations for G^E/x_1x_2RT given by ratios of polynomials. They provide great flexibility in the fitting of VLE data for binary systems. However they have scant theoretical foundation, and therefore fail to admit a rational basis for extension to multicomponent systems. [18]

4.4 Local Composition Modes

Theoretical developments in the molecular thermodynamics if liquid solution behavior is often based on the concept of 'local composition'. Within a liquid solution, local compositions, are different from the overall mixture composition, are presumed to account for the short range order and non-random molecular orientations that results from

differences in molecular size and intermolecular forces. The concept was introduced by G.M. Wilson in 1964 with publication of a model of solution behavior since known as the Wilson equation [11]. The success of this equation is the correlation of VLE data prompted the development of alternative local-composition models, most notably the NRTL (Non Random Two Liquid) equation of Renon and Prausnitz [14]. And the UNIQUAC (UNIversal QUAsi-Chemical) equation of Abrams and Prausnitz. [16]. A further significant development, based on the UNIQUAC equation, is the UNIFAC method [17]. in which activity coefficients are calculated from the contributions of the various-groups making up the molecules of a solution.

The Wilson equation, like the Margules and van Laar equations, contains just two parameters for a binary system (Λ_{12} and Λ_{21}), and is written as

$$G^E/RT = -x_1 \ln(x_1 + x_2 \Lambda_{12}) - x_2 \ln(x_2 + x_1 \Lambda_{21}) \quad \text{.....(4.7)}$$

$$\ln \gamma_1 = -\ln(x_1 + x_2 \Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x1 + x2\,\Lambda_{12}} - \frac{\Lambda_{21}}{x2 + x1\,\Lambda_{21}} \right) \quad \text{.....(4.8)}$$

$$\ln \gamma_2 = -\ln(x_2 + x_1 \Lambda_{21}) - x_1\left(\frac{\Lambda_{12}}{x1 + x2\,\Lambda_{12}} - \frac{\Lambda_{21}}{x2 + x1\,\Lambda_{21}} \right) \quad \text{.....(4.9)}$$

For infinite dilution, these equations become:

$$\ln \gamma_1^{\infty} = -\ln \Lambda_{12} + 1 - \Lambda_{21} \quad \text{and} \quad \ln \gamma_2^{\infty} = -\ln \Lambda_{21} + 1 - \Lambda_{12} \quad \text{..... (4.10) \& (4.11)}$$

Note that Λ_{12} and Λ_{21} must always be positive numbers.
The NRTL equation, containing three parameters for a binary system, is

$$G^E/ x_1 x_2 RT = \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{12}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{21}} \quad \text{.....(4.12)}$$

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{21})^2} \right] \quad \text{.....(4.13)}$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad \text{..... (4.14)}$$

Here, $G_{12} = \exp(-\alpha\tau_{12})$ $G_{21} = \exp(-\alpha\tau_{21})$ …….(4.15) & (4.16)

And $\tau_{12} = b_{12}/RT$ $\tau_{21} = b_{21}/RT$ …...(4.17) & (4.18)

Where α, b_{12} and b_{21} , parameters specific to a particular pair of species, are independent of composition and temperature. The infinite-dilution values of the activity coefficients are given by the equations:

$$\ln \gamma_1^{\infty} = \tau_{21} + \tau_{12} \exp(-\alpha\tau_{12}) \text{ and } \ln \gamma_2^{\infty} = \tau_{12} + \tau_{21} \exp(-\alpha\tau_{21}) \quad \ldots(4.19) \& (4.20)$$

The UNIQUAC equation and the UNIFAC method are models of greater complexity.

The local composition models have limited flexibility in the fitting of data, but they are adequate for most engineering purposes. Moreover, they are implicitly generalizable to multi component systems without introduction of any parameters beyond those required to describe the constituent binary systems. For example, the Wilson equation for multicomponent systems is:

$$G^E/RT = -\sum_i xi \ln \left(\sum_j x_j \Lambda_{ij} \right) \quad (4.21)$$

$$\ln \gamma_i = 1 - \ln \left(\sum_j x_j \Lambda_{ij} \right) - \sum_k x_k \Lambda_{ki} \Big/ \sum_j x_j \Lambda_{kj} \quad (4.22)$$

$\Lambda_{ij} = 1$ for i = j, etc. All indices refer to the same species, and summations are over *all* species. For each ij pair there are two parameters, because $\Lambda_{ij} \neq \Lambda_{ji}$. For a ternary system the three ij pairs are associated with the parameters Λ_{12} , Λ_{21} ; Λ_{13}, Λ_{31} ; and Λ_{23}, Λ_{32}.

The temperature dependence of the parameters is given by:

$$\Lambda_{ij} = V_j / V_i \left\{ \frac{\exp(-aij)}{RT} \right\} \quad (i \neq j) \qquad \ldots\ldots..(4.23)$$

Where V_j and V_i are the molar volumes at temperature T of pure liquids j and i, and aij is a constant independent of composition and temperature. Thus the Wilson equation, like all other local-composition models, has built into it approximate temperature dependence for the parameters. Moreover, all parameters are found from data for binary (in contrast

to multi-component) systems. This makes parameter determination for the local-composition models a task of manageable proportions [18].

4.5 SAMPLE CALCULATION

Calculation of activity coefficient

$y_i = x_i \gamma_i p_i^{sat}$

at azeotropic condition

$x_i = y_i$

so, $\gamma_i = P_T / P_i^{sat}$

Calculation of vapour phase

Using Antoine equation

$$\log P_i^{sat} = A - B/(T+C) \qquad \text{…….(4.24)}$$

Replacement of activity coefficient to VLE Model

Margules equation

$$\ln \gamma_1^* = x_2^2[A_{12} + 2(A_{21}-A_{12})x_1] \qquad \text{…….(4.25)}$$

$$\ln \gamma_2^* = x_1^2[A_{21} + 2(A_{12}-A_{21})x_2] \qquad \text{……(4.26)}$$

γ_1^* and γ_2^* are theoretical values of activity coefficients derived from the experimental values. The procedure is as follows

Methanol	Ethyl Acetate
A=7.8975	A=7.0981
B=1474.08	B=1238.71
C=229.13	C=217.10

Now, for different values of T we can calculate P_i^{sat}

Gibbs Energy

$G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$ ……..(4.27)

And by Margules equation method $G^E/x_1x_2RT = A_{21}x_1 + A_{12}x_2$ ……(4.28)

Now $\ln \gamma_1^{\infty} = A_{12}$ and $\ln \gamma_2^{\infty} = A_{21}$ which are obtained by plotting curve $\ln \gamma_1$, $\ln \gamma_2$ vs x_1
So now by putting the values of A_{12} and A_{21} the theoretical γ_1^* and γ_2^* can be found out and thereby by the following relations theoretical vapour composition y_1^* and y_2^* can be obtained.

$$y_1^* = x_1 \gamma_1 P_1^{sat} / (x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}) \quad \text{……(4.29)}$$

$$y_2^* = x_2 \gamma_2 P_2^{sat} / (x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}) \quad \text{…….(4.30)}$$

All the values given above have been calculated and tabulated [25].

4.6 Results and Discussion

The VLE data for the present binary system was obtained at atmospheric condition of 98.6 ± 0.03 kpa pressure.

In the present Methanol (1) Ethyl Acetate (2) system , it has been observed that the system forms a minimum boiling azeotrope 0.732 mole fraction of methanol at 62.6°C. The salts which have been used to study the salt effect on the system are Lithium Chloride and Lithium Bromide.

It has been found out that salting –in and salting-out of methanol has been seen in the case of Lithium Bromide whereas during the study for the salt Lithium Chloride only salting-in of methanol was observed. This is due to the changes of relative volatility of the binary system with the solid salts. Apparently the salt effect increases as we increase the concentration of salts as by the addition of salts like Lithium Chloride and Lithium Bromide, it has been found that the azeotrope shifts but the azeotropy couldn't be eliminated even with addition of higher concentrations of salts. The azeotrope shifts from 0.732 to 0.629, 0,586, 0.472 and 0.471 by addition of 5%, 10%, 15% and 20% of lithium chloride salt respectively and to 0.774, 0,706, 0.682, 0.670 by the addition of 5%, 10%, 15% and 20% lithium bromide respectively. From this data it has been found that Lithium Chloride is more effective than Lithium Bromide.

TABULATION

TABLE 4-
REFRACTIVE INDEX DATA
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
SALT: LITHIUM CHLORIDE

Liquid composition X_1	**Liquid phase refractive index (on salt free basis)**	**Salt (0%)**		**Salt (5%)**		**Salt (10%)**		**Salt (15%)**		**Salt (20%)**	
		u_x	**T**	**u_x**	**T**	**u_x**	**T**	**u_x**	**T**	**u_x**	**T**
0	1.3689	1.3689	77.1	1.3685	77.1	1.3685	77.1	1.3685	77.1	1.3685	77.1
0.1	1.3679	1.3635	70.5	1.3605	70	1.3572	69.6	1.3535	69.5	1.3526	69.5
0.2	1.3655	1.3524	66.5	1.3521	65.9	1.3491	65.8	1.3471	65.9	1.3458	65.9
0.3	1.3622	1.3510	63.7	1.3476	63.4	1.3484	63.4	1.3518	63.3	1.3510	63.5
0.4	1.3586	1.3494	62.8	1.3474	62.7	1.3512	62.7	1.3588	62.8	1.3586	62.7
0.5	1.3548	1.3489	62.0	1.3496	61.8	1.3540	61.8	1.3630	61.7	1.3632	61.7
0.6	1.3523	1.3481	62.7	1.3521	62.7	1.3548	62.7	1.3638	62.7	1.3642	62.9
0.7	1.3481	1.3476	62.4	1.3532	62.6	1.3527	62.8	1.3609	62.9	1.3616	62.9
0.8	1.3433	1.3462	62.5	1.3512	62.6	1.3472	63.0	1.3531	63.0	1.3540	63.1
0.9	1.3355	1.3403	62.8	1.3435	62.9	1.3385	63.2	1.3402	63.4	1.3410	63.4
1	1.3265	1.3263	64.7	1.3265	64.7	1.3265	64.7	1.3265	64.7	1.3265	64.7

TABLE 5-
REFRACTIVE INDEX DATA
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
SALT: LITHIUM BROMIDE

Liquid composition X_1	Liquid phase refractive index (on salt free basis)	Salt (0%)		Salt (5%)		Salt (10%)		Salt (15%)		Salt (20%)	
		u_x	T	u_x	T	u_x	T	u_x	T	u_x	T
0	1.3689	1.3689	77.1	1.3689	77.1	1.3689	77.1	1.3689	77.1	1.3689	77.1
0.1	1.3679	1.3635	70.5	1.3618	70.5	1.3566	70.4	1.3535	70.2	1.3523	70
0.3	1.3622	1.3510	63.7	1.3427	65.9	1.3393	65.9	1.3380	65.9	1.3357	65.8
0.5	1.3548	1.3489	62.0	1.3412	63.1	1.3410	64.3	1.3406	64.8	1.3398	65.3
0.7	1.3481	1.3476	62.4	1.3451	64	1.3468	63.9	1.3478	63.1	1.3492	64.3
0.9	1.3355	1.3403	62.8	1.335	62.6	1.3368	63	1.3412	64.3	1.3426	65
1	1.3265	1.3265	64.7	1.3265	64.7	1.3265	64.7	1.3265	64.7	1.3265	64.7

TABLE 6-
VAPOUR EQUILIBRIUM DATA
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
SALT: LITHIUM CHLORIDE

Serial no	Liquid composition	Vapour Phase Composition				
		Salt (0%)	Salt (5%)	Salt (10%)	Salt (15%)	Salt (20%)
	X_1	Y_1	Y_1	Y_1	Y_1	Y_1
1	0	0.000	0.000	0.000	0.000	0.000
2	0.1	0.287	0.389	0.494	0.600	0.625
3	0.2	0.631	0.640	0.713	0.759	0.786
4	0.3	0.667	0.747	0.730	0.647	0.668
5	0.4	0.706	0.752	0.660	0.447	0.453
6	0.5	0.718	0.702	0.586	0.306	0.299
7	0.6	0.736	0.639	0.564	0.278	0.262
8	0.7	0.747	0.610	0.622	0.377	0.353
9	0.8	0.778	0.662	0.757	0.613	0.587
10	0.9	0.889	0.832	0.917	0.890	0.877
11	1	1.000	1.000	1.000	1.000	1.000

TABLE 7-
VAPOUR EQUILIBRIUM DATA
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
SALT: LITHIUM BROMIDE

Serial no	Liquid composition	Vapour Phase Composition				
	X_1	Y_1(0% Salt)	Y_1(5% Salt)	Y_1(10% Salt)	Y_1(15% Salt)	Y_1(20% Salt)
1	0	0.000	0.000	0.000	0.000	0.000
2	0.1	0.287	0.340	0.488	0.563	0.590
3	0.3	0.667	0.775	0.833	0.855	0.891
4	0.5	0.718	0.801	0.804	0.811	0.825
5	0.7	0.747	0.733	0.701	0.682	0.654
6	0.9	0.889	0.901	0.844	0.801	0.777
7	1	1.000	1.000	1.000	1.000	1.000

TABLE 8-
CALCULATION OF ACTIVITY CO-EFFICIENT
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
NO SALT

Serial no	(X_1)	T	P_1	P_2	γ_1	γ_2	ln γ_1	ln γ_2
1	0.1	70.5	126.28	80.52	2.245	0.970	0.809	-0.030
2	0.2	66.5	109.57	70.66	2.839	0.645	1.044	-0.439
3	0.3	63.7	97.87	63.76	2.240	0.737	0.807	-0.305
4	0.4	62.8	94.12	61.54	1.850	0.786	0.615	-0.241
5	0.5	62	90.77	59.57	1.560	0.935	0.445	-0.067
6	0.6	62.7	93.70	61.30	1.292	1.061	0.256	0.060
7	0.7	62.4	92.44	60.56	1.140	1.371	0.131	0.316
8	0.8	62.5	92.86	60.80	1.033	1.801	0.033	0.588
9	0.9	62.8	94.12	61.54	1.035	1.785	0.034	0.579

TABLE 9-
CALCULATION OF THEORITICAL ACTIVITY CO-EFFICIENT
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
NO SALT A_{12}=-0.36,A_{21}=0.66

Serial no	Liquid composition (X_1)	$\Delta G/RTX_1X_2$	γ_{1^*}	$\ln(\gamma_{1^*})$	γ_{2^*}	$\ln(\gamma_{2^*})$
1	0.1	8.053	0.881	-0.126	0.988	-0.012
2	0.2	4.669	1.031	0.031	0.962	-0.039
3	0.3	2.252	1.131	0.123	0.933	-0.069
4	0.4	1.136	1.178	0.164	0.914	-0.090
5	0.5	0.755	1.179	0.165	0.914	-0.090
6	0.6	0.576	1.148	0.138	0.945	-0.056
7	0.7	1.239	1.101	0.096	1.024	0.024
8	0.8	2.983	1.052	0.051	1.175	0.161
9	0.9	5.833	1.015	0.015	1.447	0.369

TABLE 10-
ACTIVITY CO-EFFICIENT
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
LITHIUM CHLORIDE

(X1)	5% Salt				10% Salt				15% Salt				20% Salt			
	γ_1	γ_2	γ_1^*	γ_2^*	γ_1	γ_2	γ_1^*	γ_2^*	γ_1	γ_2	γ_1^*	γ_2^*	γ_1	γ_2	γ_1^*	γ_2^*
0.1	3.087	0.845	0.848	0.983	3.976	0.709	0.829	0.981	4.850	0.561	0.729	0.975	5.049	0.527	0.707	0.973
0.2	2.947	0.643	1.067	0.944	3.296	0.514	1.063	0.940	3.496	0.430	1.026	0.919	3.623	0.381	1.015	0.914
0.3	2.543	0.566	1.221	0.904	2.485	0.603	1.231	0.896	2.211	0.793	1.259	0.860	2.263	0.740	1.263	0.852
0.4	1.981	0.664	1.293	0.878	1.739	0.911	1.311	0.868	1.170	1.479	1.383	0.819	1.192	1.468	1.397	0.808
0.5	1.540	0.996	1.290	0.880	1.286	1.382	1.310	0.869	0.674	2.328	1.394	0.815	0.659	2.352	1.412	0.803
0.6	1.121	1.453	1.236	0.929	0.990	1.753	1.253	0.920	0.489	2.904	1.325	0.869	0.456	2.944	1.341	0.857
0.7	0.922	2.101	1.158	1.051	0.932	2.019	1.169	1.048	0.562	3.318	1.218	1.020	0.526	3.446	1.228	1.012
0.8	0.875	2.734	1.081	1.298	0.983	1.936	1.086	1.312	0.796	3.079	1.110	1.351	0.759	3.274	1.116	1.356
0.9	0.965	2.681	1.023	1.783	1.050	1.305	1.024	1.839	1.010	1.716	1.031	2.073	0.995	1.932	1.032	2.121

TABLE 11-
ACTIVITY CO-EFFICIENT
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
LITHIUM BROMIDE

(X1)	**5% Salt**				**10% Salt**				**15% Salt**				**20% Salt**			
	γ_1	γ_2	γ_1^*	γ_2^*	γ_1	γ_2	γ_1^*	γ_2^*	γ_1	γ_2	γ_1^*	γ_2^*	γ_1	γ_2	γ_1^*	γ_2^*
0.1	2.656	0.899	0.937	0.993	3.825	0.699	0.918	0.989	4.443	0.600	0.902	0.987	4.687	0.567	0.887	0.986
0.3	2.381	0.458	1.082	0.961	2.559	0.340	1.148	0.940	2.626	0.295	1.179	0.929	2.748	0.223	1.202	0.919
0.5	1.657	0.630	1.105	0.951	1.580	0.593	1.182	0.928	1.562	0.561	1.221	0.914	1.557	0.510	1.252	0.903
0.7	1.042	1.361	1.059	1.020	1.001	1.530	1.100	1.044	1.008	1.679	1.120	1.052	0.918	1.744	1.137	1.057
0.9	1.059	1.600	1.009	1.255	0.974	2.481	1.015	1.470	0.875	3.009	1.017	1.584	0.825	3.285	1.020	1.677

TABLE 12-
CALCULATED AND THEORITICAL VAPOUR COMPOSITION
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
LITHIUM CHLORIDE

X_1	Vapour composition- Y_1 (experimental)					Vapour composition- Y_1 (theoretical)				
	0% salt	5% salt	10% salt	15% salt	20% salt	0% salt	5% salt	10% salt	15% salt	20% salt
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.1	0.287	0.389	0.494	0.600	0.625	0.134	0.131	0.128	0.115	0.112
0.2	0.631	0.640	0.713	0.759	0.786	0.294	0.304	0.304	0.302	0.301
0.3	0.667	0.747	0.730	0.647	0.668	0.444	0.470	0.474	0.490	0.494
0.4	0.706	0.752	0.660	0.447	0.453	0.568	0.600	0.606	0.633	0.638
0.5	0.718	0.702	0.586	0.306	0.299	0.663	0.691	0.696	0.723	0.728
0.6	0.736	0.639	0.564	0.278	0.262	0.736	0.753	0.757	0.778	0.782
0.7	0.747	0.610	0.622	0.377	0.353	0.793	0.797	0.799	0.810	0.812
0.8	0.778	0.662	0.757	0.613	0.587	0.845	0.836	0.835	0.834	0.834
0.9	0.889	0.832	0.917	0.890	0.877	0.906	0.888	0.885	0.873	0.870
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TABLE 13-
CALCULATED AND THEORITICAL VAPOUR COMPOSITION
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
LITHIUM BROMIDE

X_1	Vapour composition- Y_1 (experimental)					Vapour composition- Y_1 (theoretical)				
	0% salt	5% salt	10% salt	15% salt	20% salt	0% salt	5% salt	10% salt	15% salt	20% salt
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.1	0.287	0.340	0.488	0.563	0.590	0.134	0.141	0.139	0.137	0.135
0.3	0.667	0.775	0.833	0.855	0.891	0.444	0.427	0.448	0.457	0.464
0.5	0.718	0.801	0.804	0.811	0.825	0.663	0.640	0.662	0.673	0.682
0.7	0.747	0.733	0.701	0.682	0.654	0.793	0.788	0.791	0.792	0.794
0.9	0.889	0.901	0.844	0.801	0.777	0.906	0.917	0.905	0.899	0.894
1	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TABLE 14-
ERROR CALCULATION
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
LITHIUM CHLORIDE

Liquid composition (X_1)	**% ERROR= [(Y_1 (exp) – Y_2 (theo))/ Y_1 (exp)] * 100**				
	0% SALT	5% SALT	10% SALT	15% SALT	20% SALT
0.1	53.31%	66.32%	74.09%	80.83%	82.08%
0.2	53.41%	52.50%	57.36%	60.21%	61.70%
0.3	33.43%	37.08%	35.07%	24.27%	26.05%
0.4	19.55%	20.21%	08.18%	41.61%	40.84%
0.5	7.66%	1.57%	18.77%	76.27%	83.48%
0.6	0.14%	17.84%	34.22%	79.86%	88.47%
0.7	6.16%	30.66%	28.46%	14.85%	70.03%
0.8	8.61%	26.28%	10.30%	36.05%	42.08%
0.9	1.91%	6.73%	3.49%	1.91%	0.80%

TABLE 15-
ERROR CALCULATION
SYSTEM: METHANOL (1) + ETHYL ACETATE (2)
LITHIUM BROMIDE

Liquid composition (X_1)	**% ERROR= [(Y_1 (exp) – Y_2 (theo))/ Y_1 (exp)] * 100**				
	0% SALT	5% SALT	10% SALT	15% SALT	20% SALT
0.1	53.31%	58.52%	71.51%	75.66%	77.11%
0.3	33.43%	44.90%	46.21%	46.54%	47.92%
0.5	1.91%	20.09%	17.66%	1.70%	17.33%
0.7	6.16%	0.75%	1.28%	1.61%	2.14%
0.9	7.66%	0.17%	0.72%	1.22%	1.50%

GRAPHS

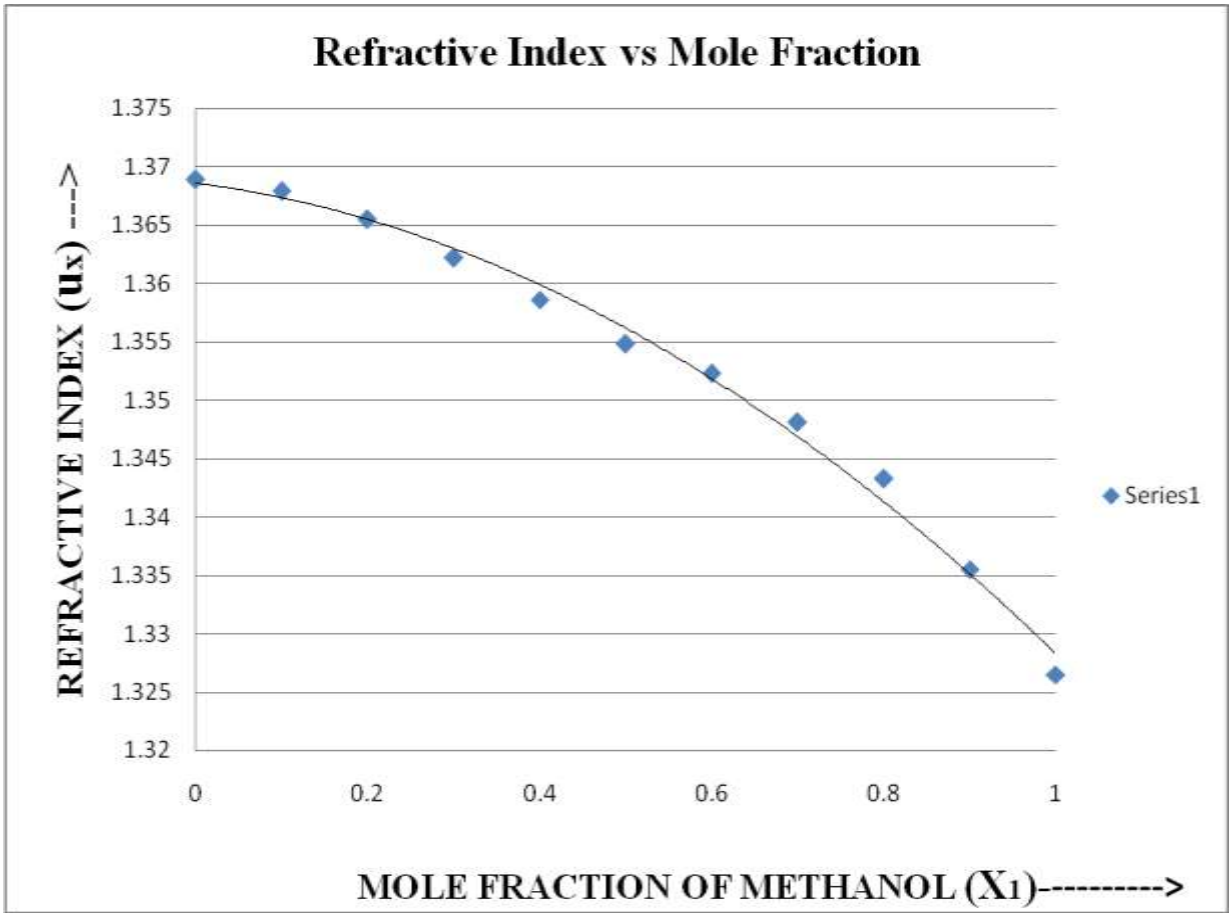


Fig 5 - Plot of Refractive Index vs Mole Fraction of methanol

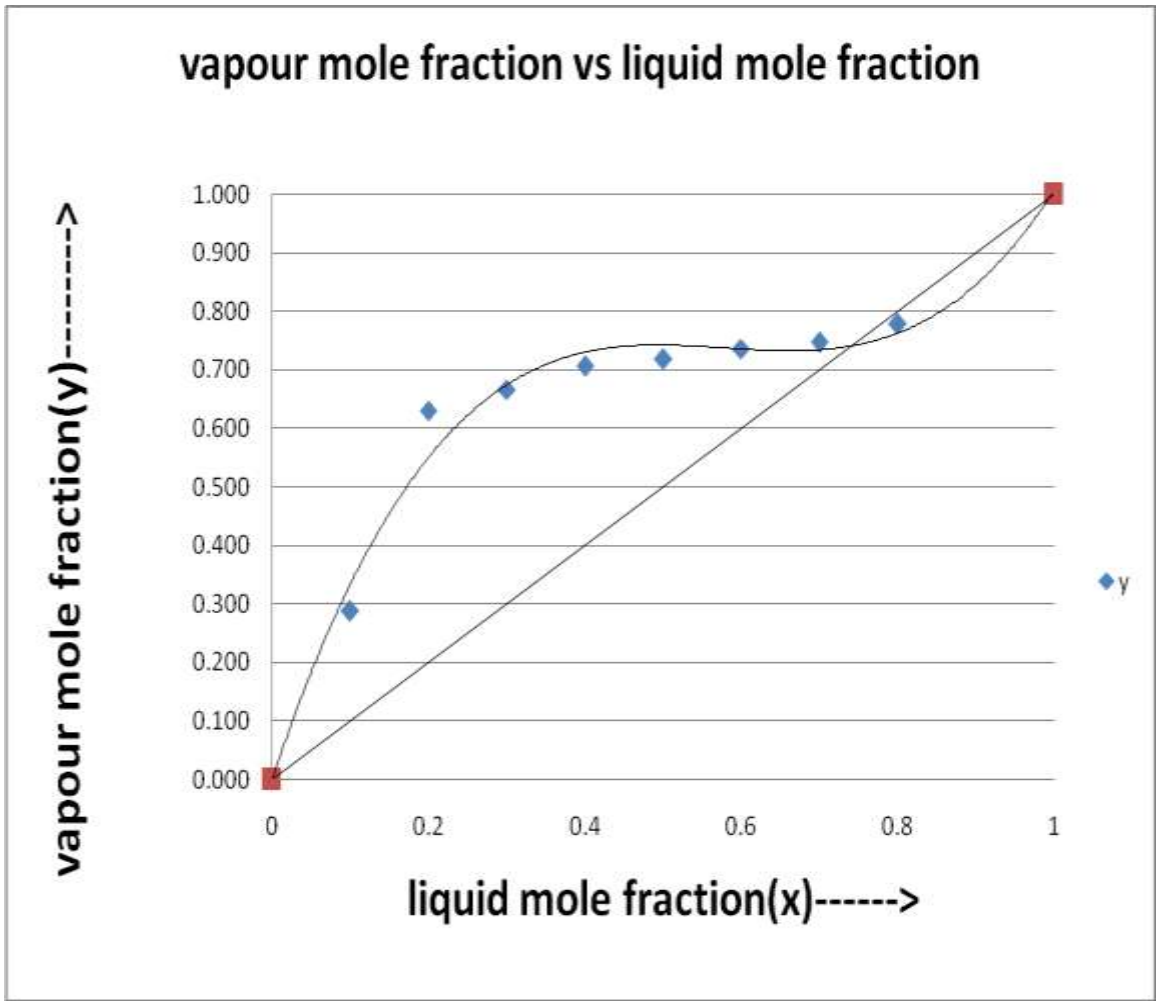


Fig 6 - **Vapour-Liquid Equilibrium Plot (0 % salt)**

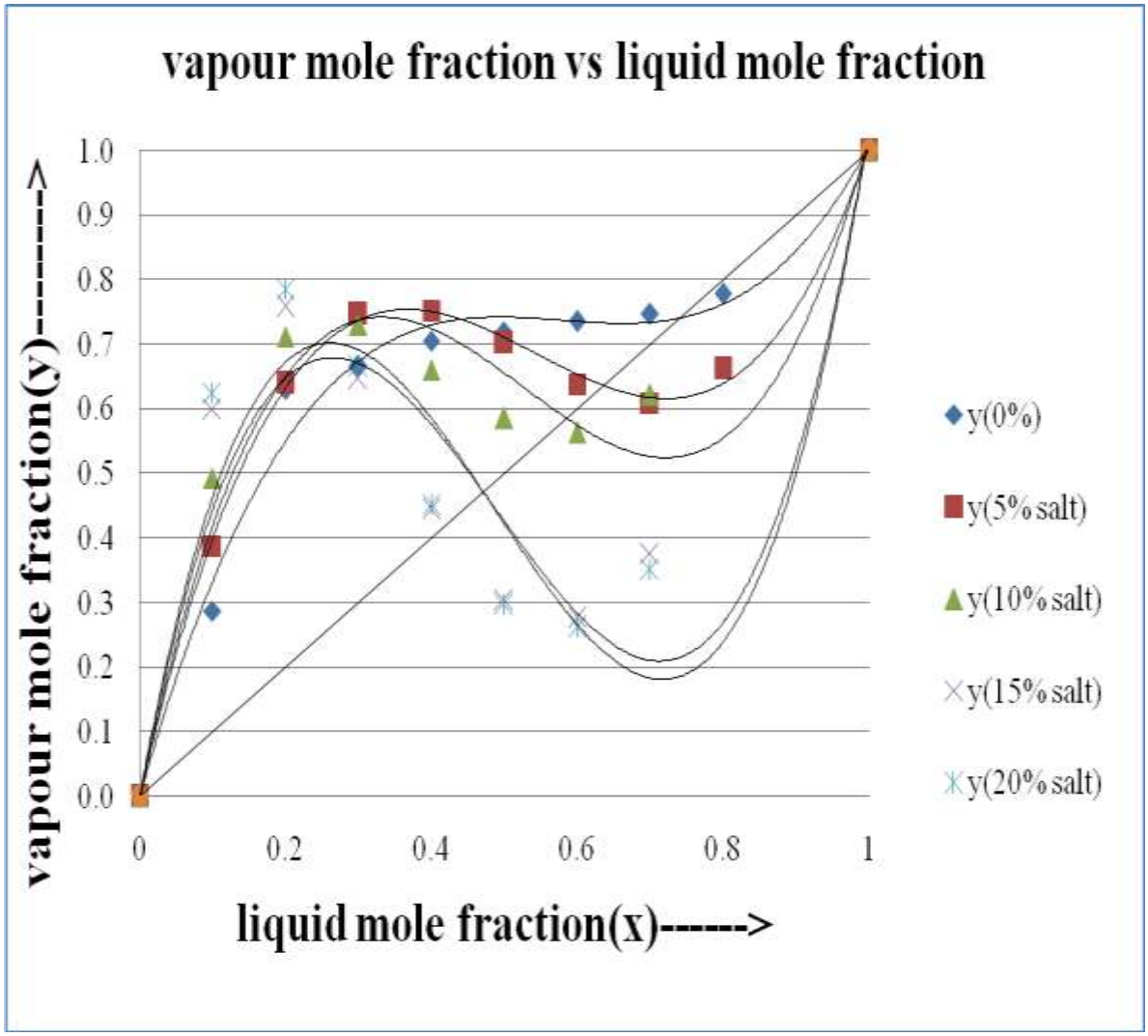


Fig 7 - **Vapour-Liquid Equilibrium Plot (Lithium Chloride)**

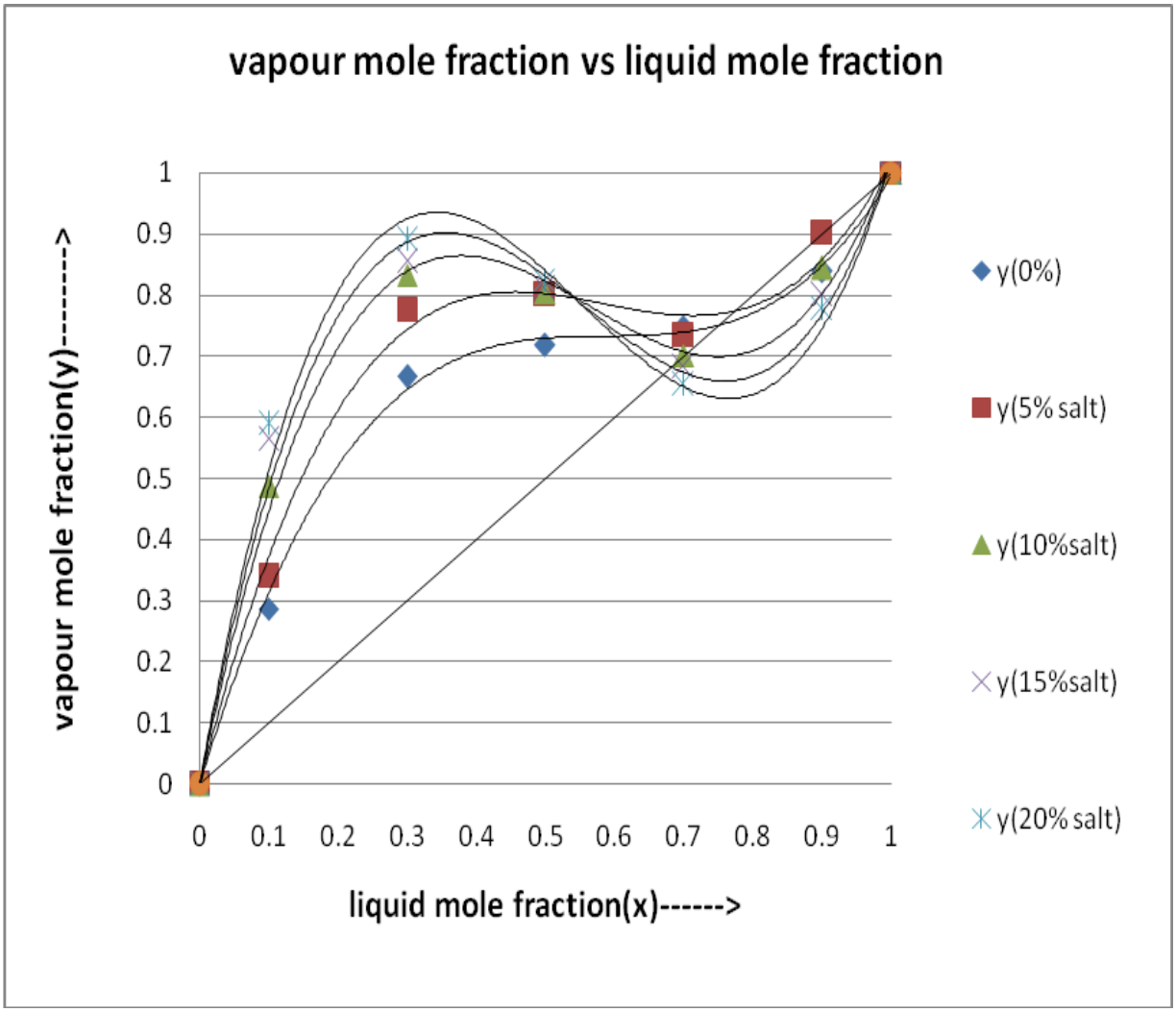


Fig 8 - **Vapour-Liquid Equilibrium Plot (Lithium Bromide)**

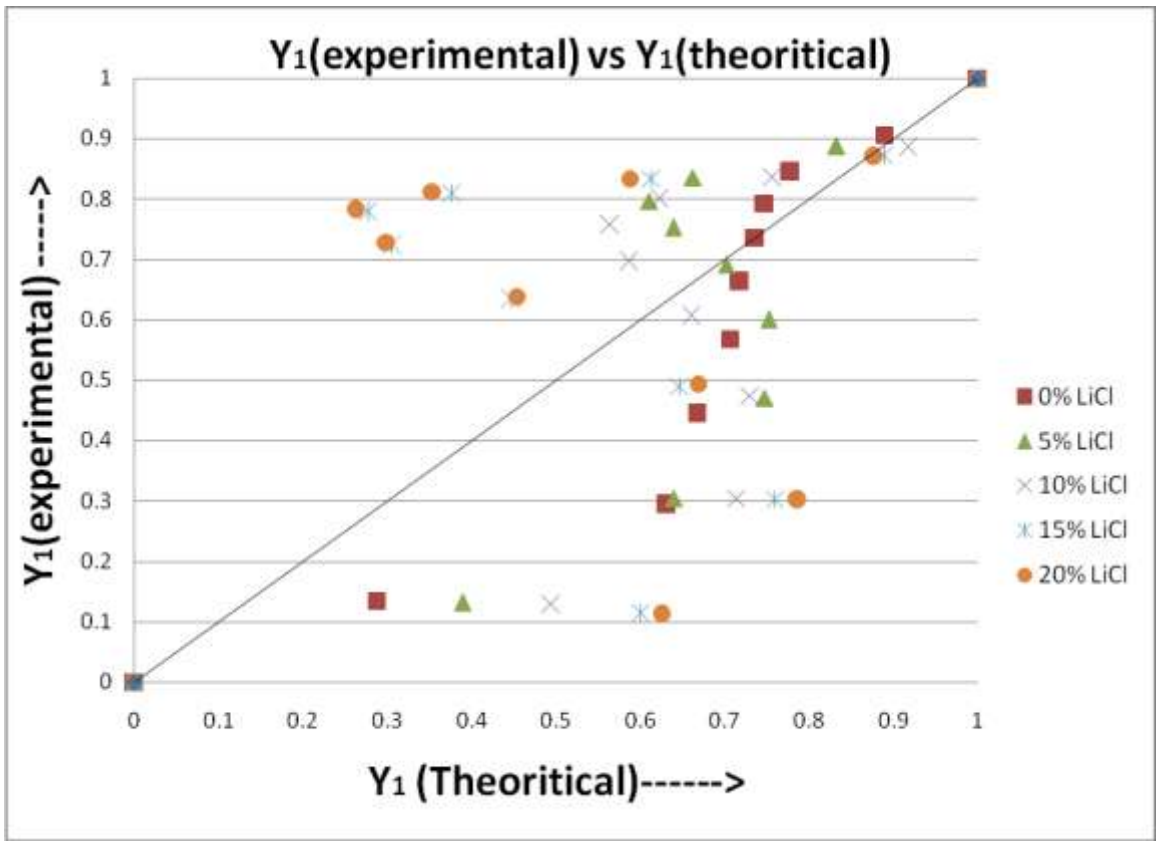


Fig 9 - Y_1(experimental) vs Y_1(theoretical) plot for LiCl

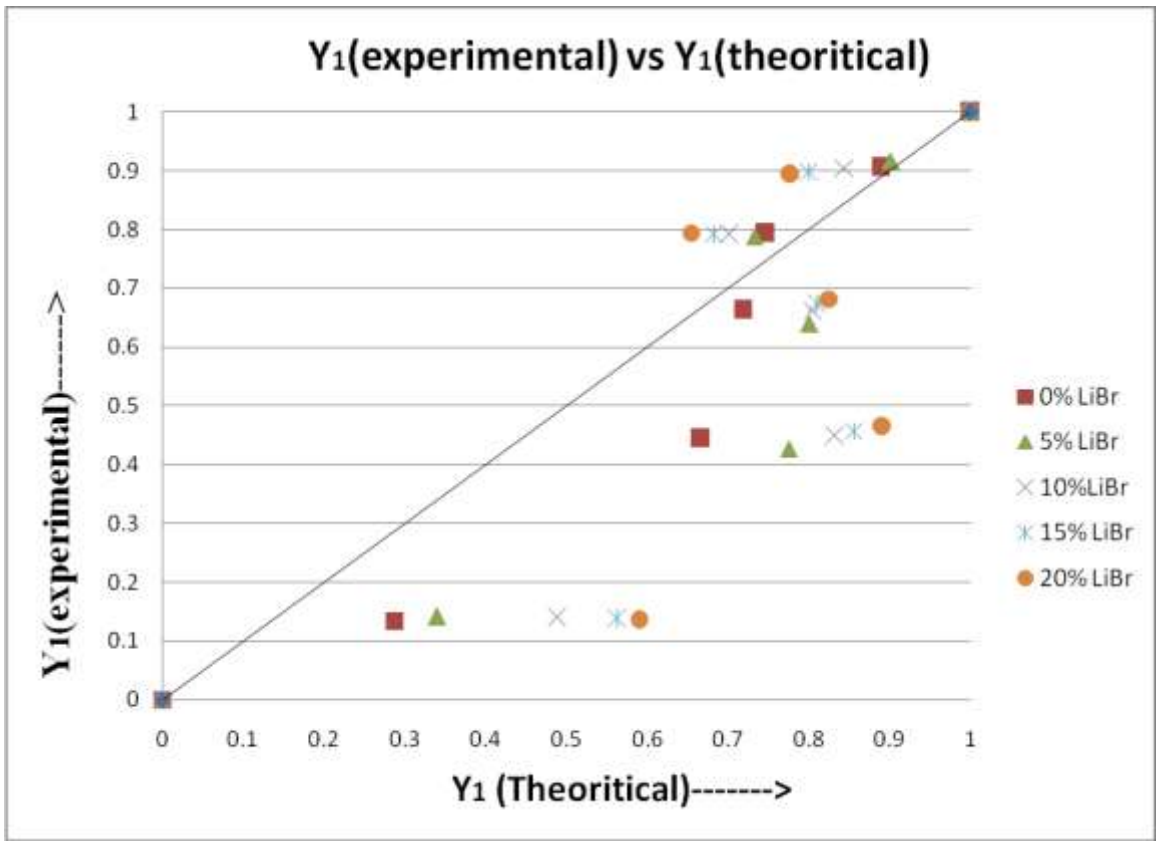


Fig 10 - Y_1(experimental) vs Y_1(theoretical) plot for LiBr

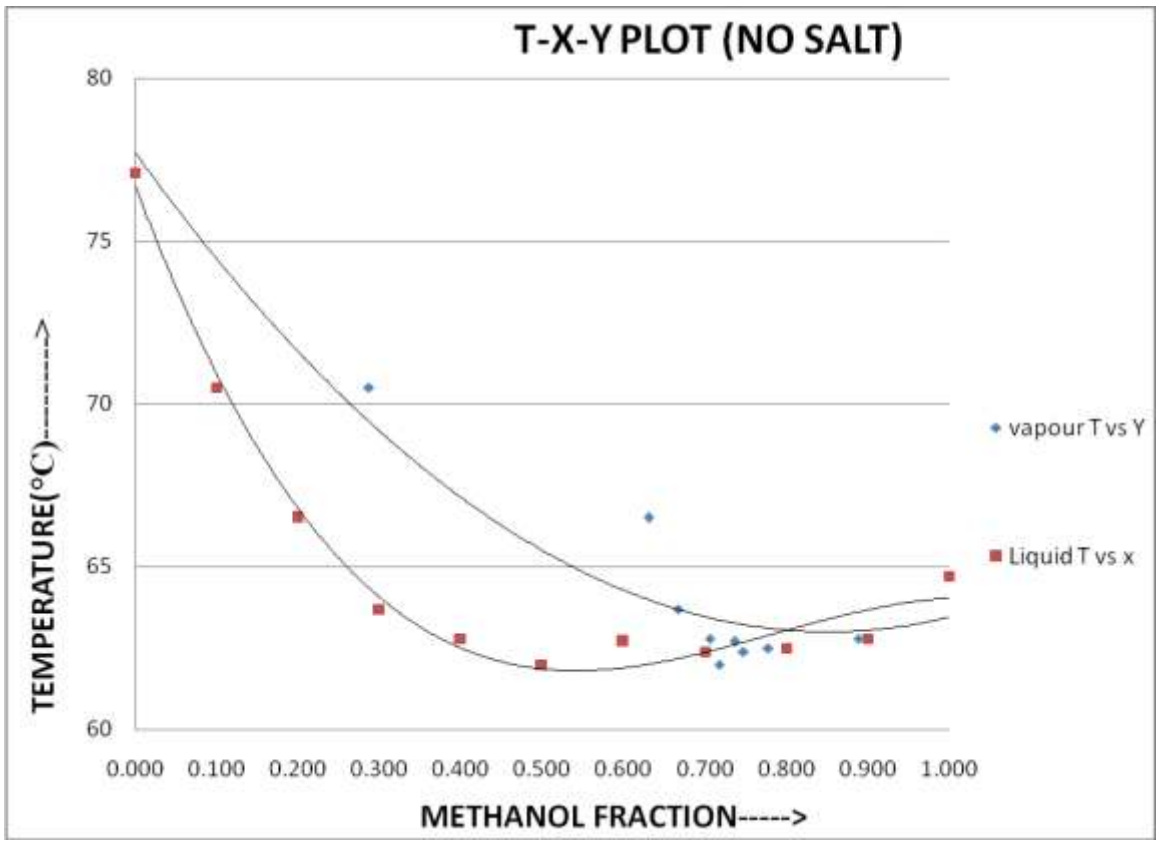


Fig 11 - T-X-Y PLOT (NO SALT)

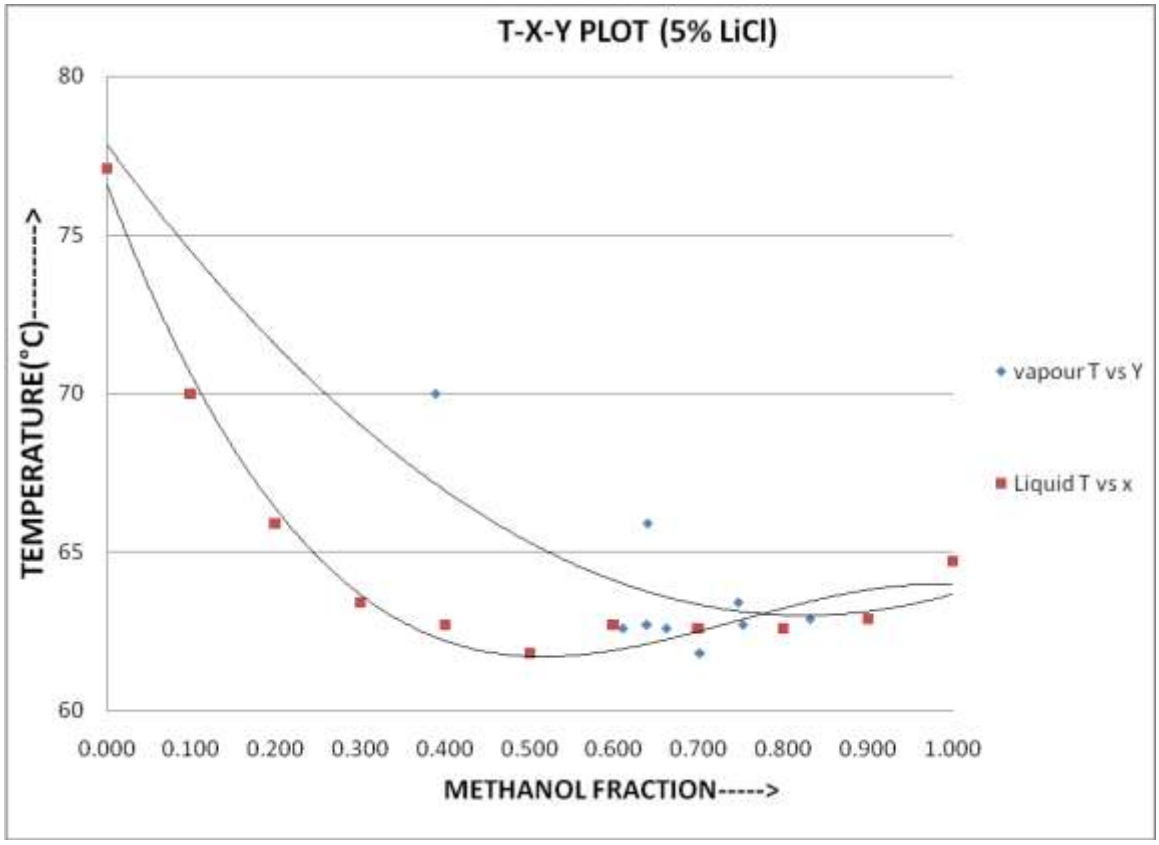


Fig 12 - T-X-Y PLOT (5% LITHIUM CHLORIDE)

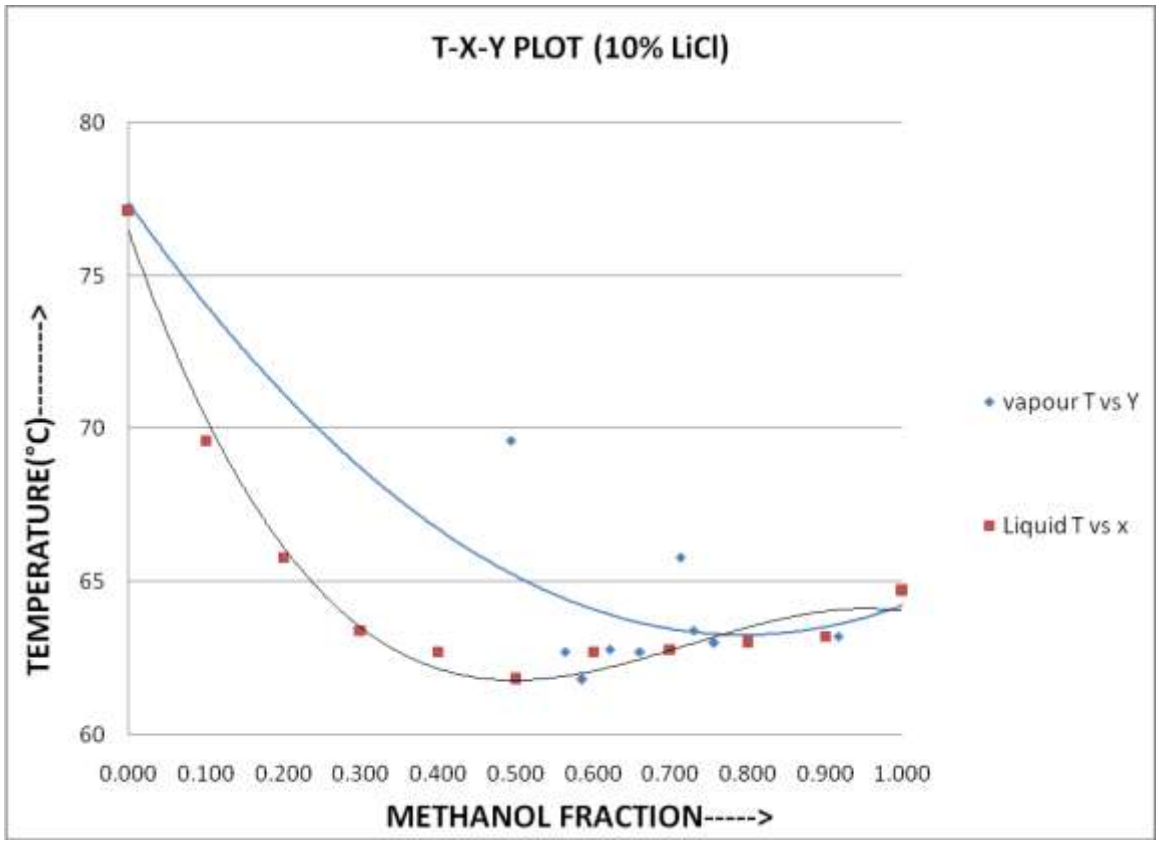


Fig 13 - T-X-Y PLOT (10% LITHIUM CHLORIDE)

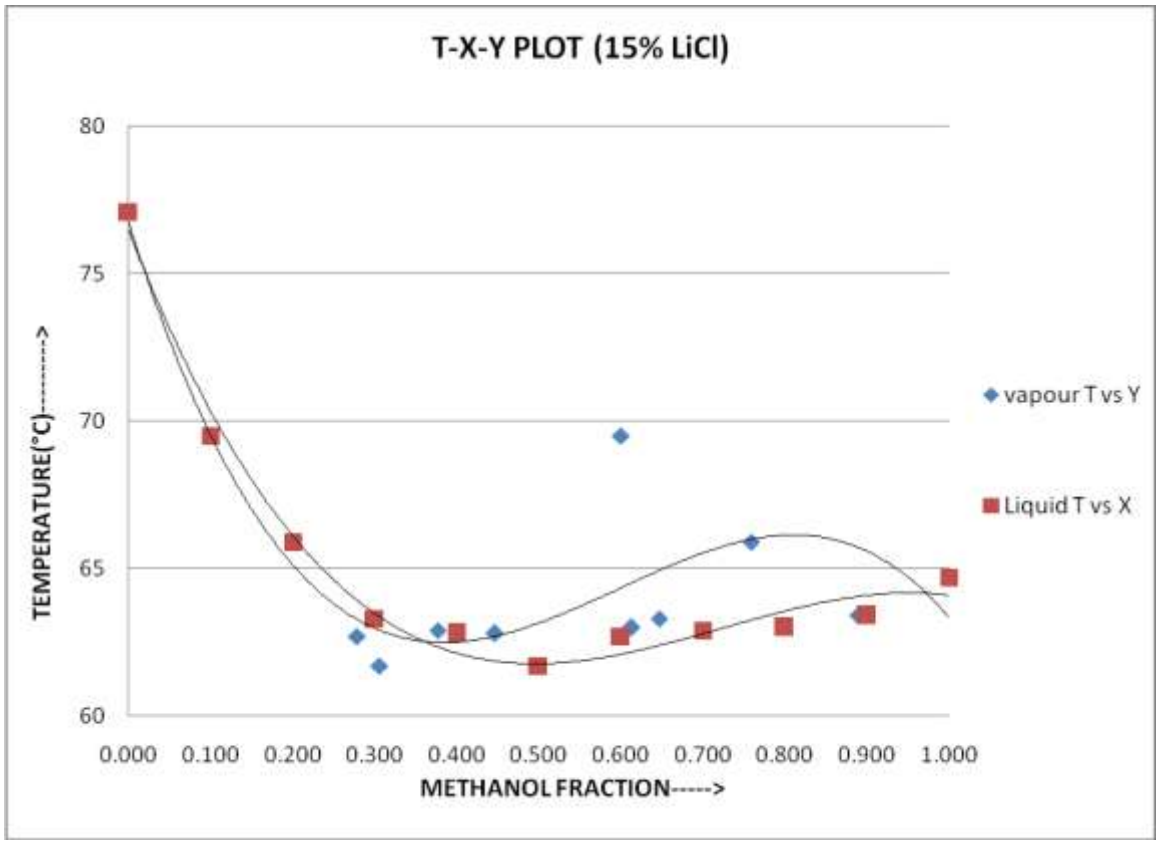


Fig 14 - T-X-Y PLOT (15% LITHIUM CHLORIDE)

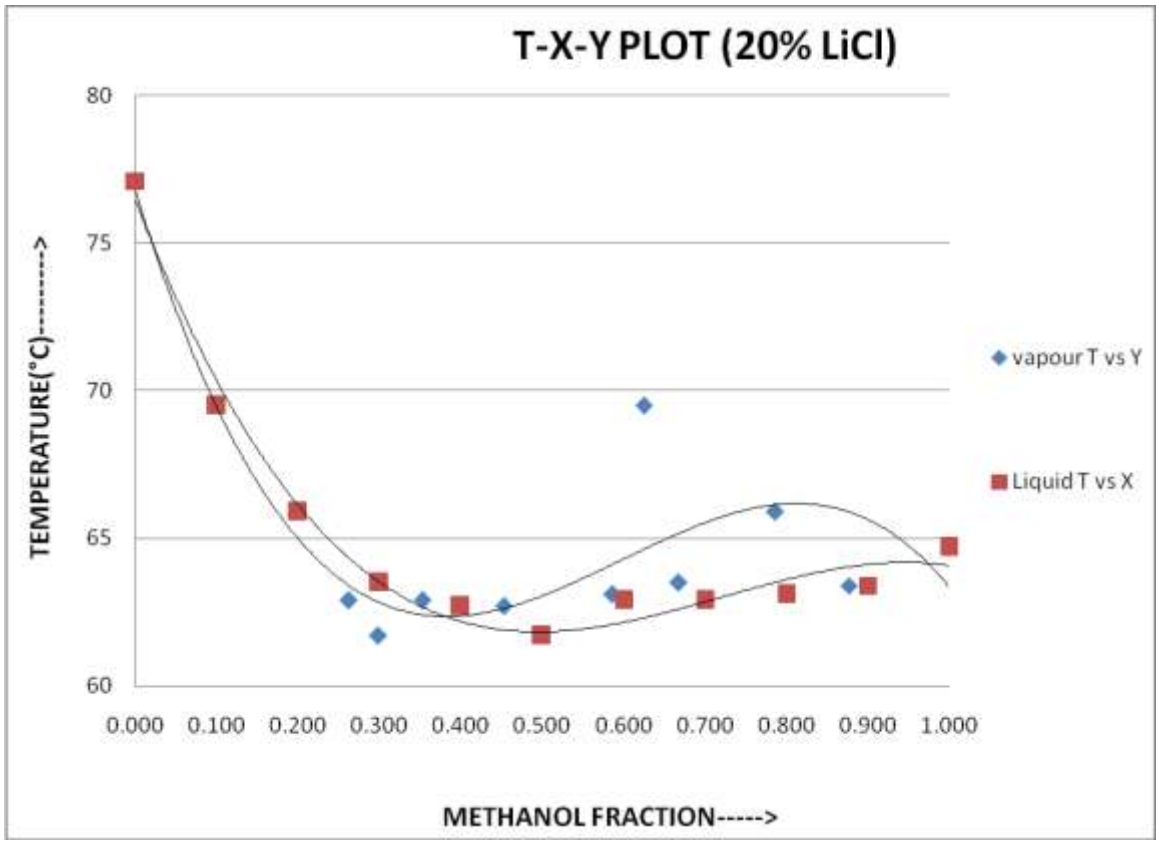


Fig 15 - T-X-Y PLOT (20% LITHIUM CHLORIDE)

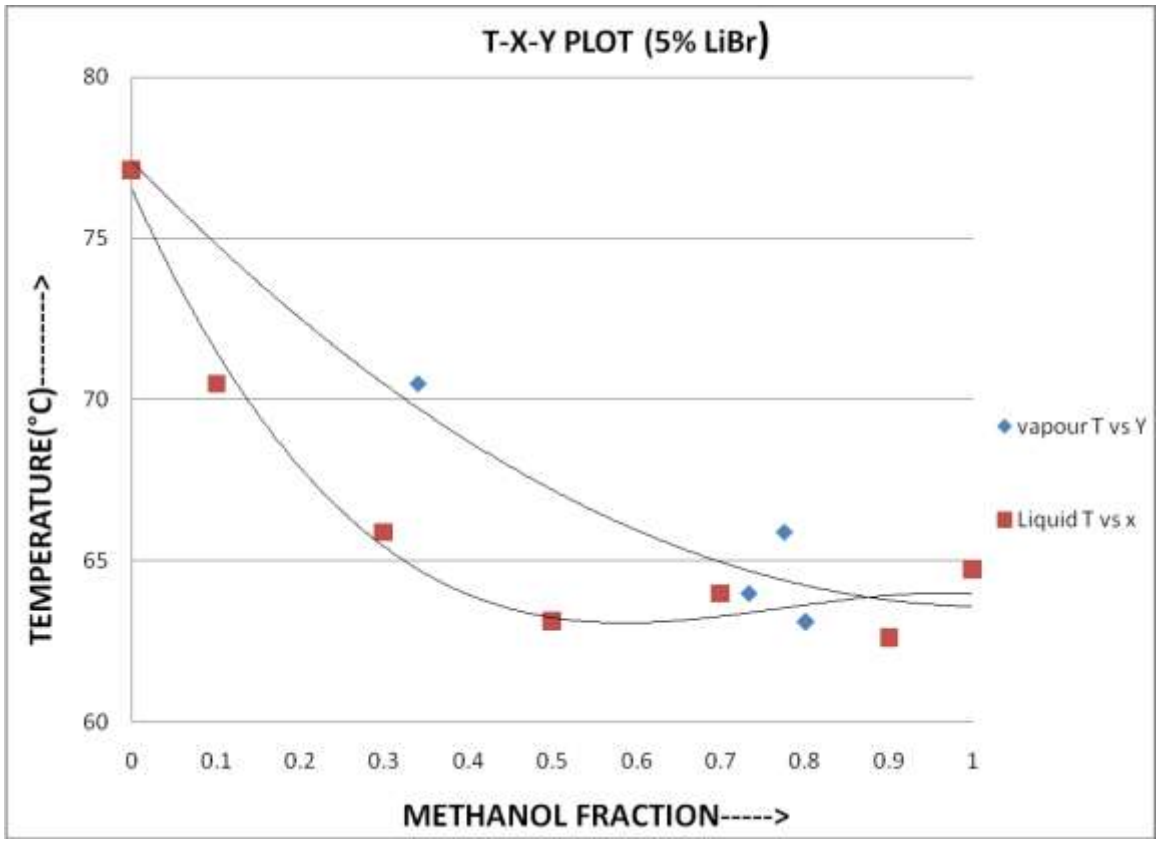


Fig 16 - T-X-Y PLOT (5% LITHIUM BROMIDE)

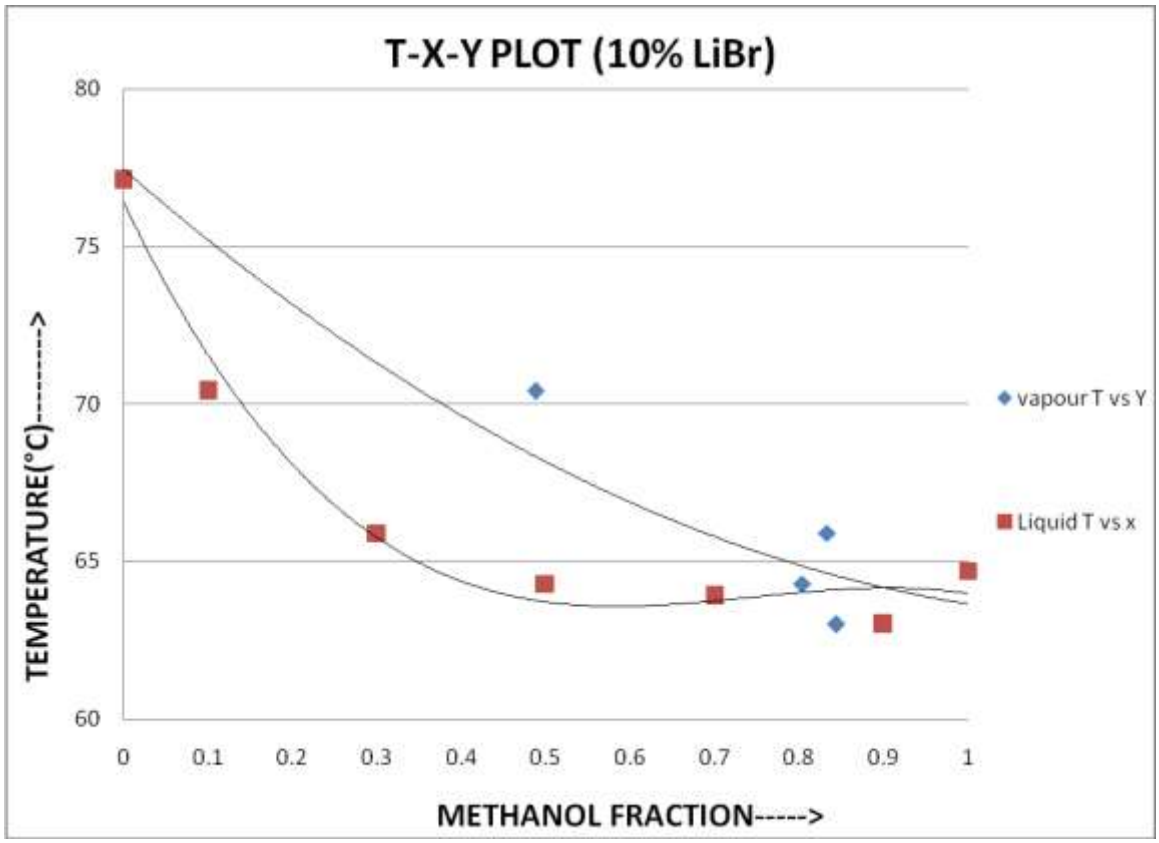


Fig 17 - T-X-Y PLOT (10% LITHIUM BROMIDE)

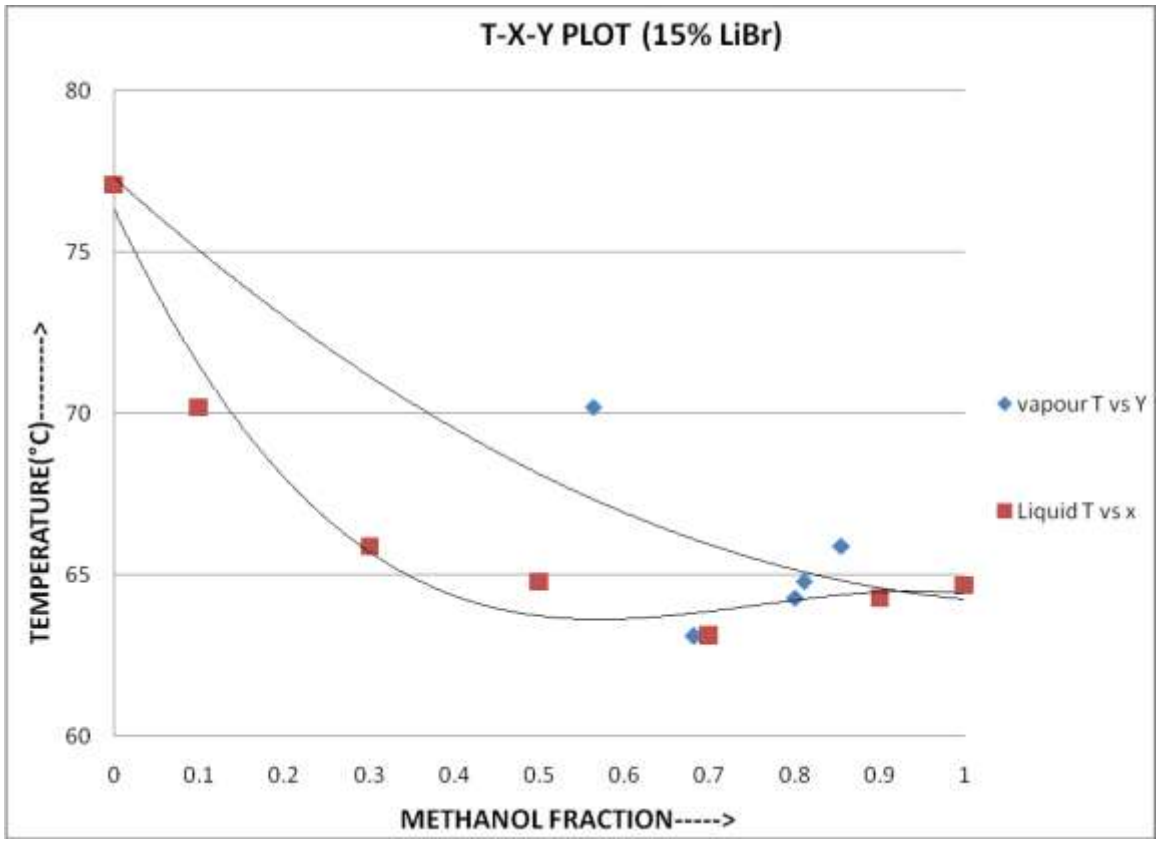


Fig 18 - T-X-Y PLOT (15% LITHIUM BROMIDE)

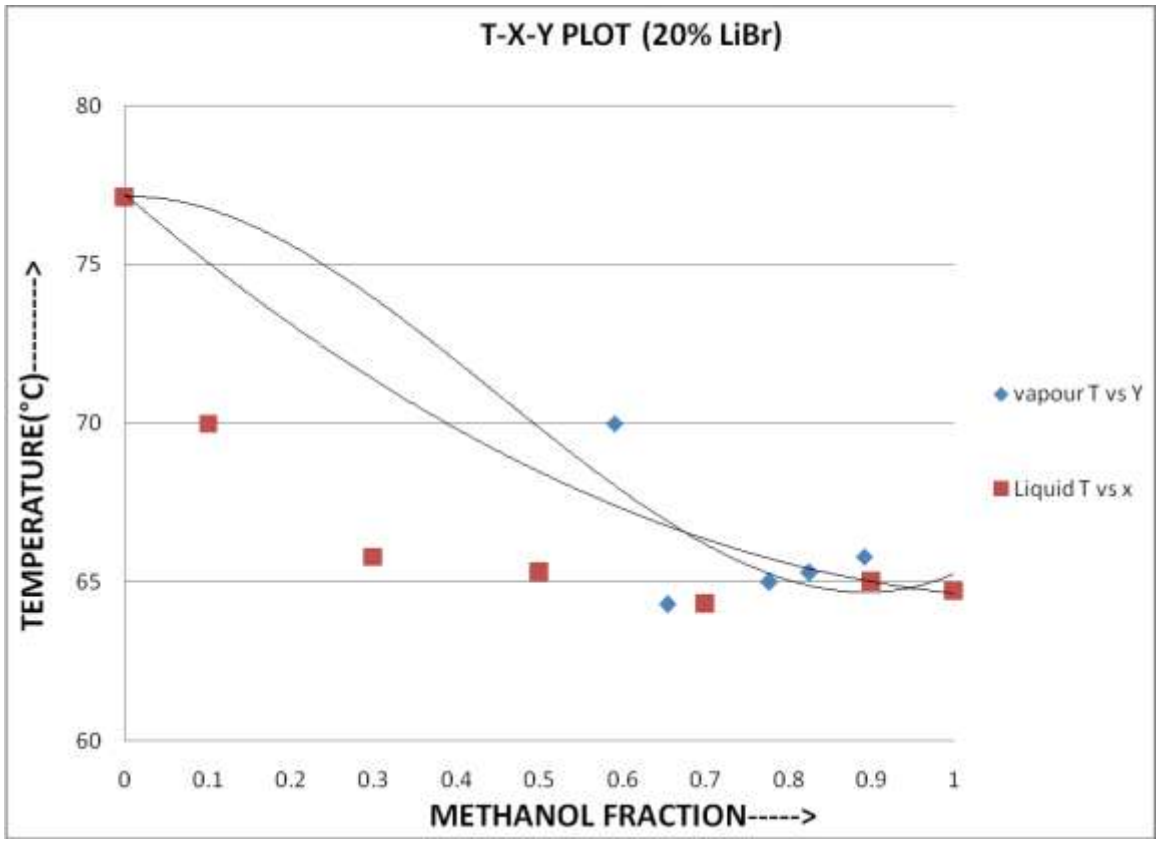


Fig 19 - T-X-Y PLOT (20% LITHIUM BROMIDE)

CHAPTER 5

CONCLUSION

In this present study the effect of solid salts on the Vapour-Liquid equilibrium relationship of a non-aqueous binary system i.e.

System: Ethyl Acetate (1) –Methanol (2) (with Salts: Lithium Chloride and Lithium Bromide) at an atmospheric pressure of 98.6 ± 0.03 kpa has been investigated.

It is concluded that the thermodynamic behavior of the system was significantly modified by the salts. It was also concluded that by using Lithium Chloride and Lithium Bromide at different concentrations e.g. 5%, 10%, 15%, and 20% by weight of methanol for the system Methanol (1) and Ethyl Acetate (2), there was a change in relative volatility in the system but the azeotropy of the system couldn't be eliminated.

The acetate group in the solution is in excess, which might have resulted in the increase of liberation of ethyl acetate to the vapor phase. Another reason could be the degree of dissociation of the salt at different composition of the liquid phase. At lower concentration of methanol it might be difficult for the solvent to dissociate the salt, but as the concentration of methanol increases, more and more salt is dissolved holding back this solvent group to give a salting in effect. Or else the liquid-liquid interaction might have not allowed the methanol to be potentially active enough to dissociate the salt in the methanol lean region, but as the methanol concentration increased with decrease in ethyl acetate concentration the opposite phenomenon was observed.

The calculation of the deviation of the experimental and the calculated data has been done as per the proposed method outlined. [22]

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